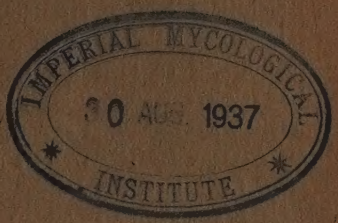
COMPTES RENDUS

(DOKLADY)

DE L'ACADÉMIE DES SCIENCES DE L'URSS

NOUVELLE SÉRIE

1937



VOLUME XVI

№ 2

ÉDITION DE L'ACADÉMIE DES SCIENCES DE L'URSS
MOSCOU

AVIS AUX AUTEURS

Les «Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS» paraissent tous les dix jours, neuf numéros formant un volume d'environ 500 pages pourvu d'une table des matières.

Les «Comptes Rendus de l'Académie des Sciences de l'URSS» publient des communications courtes précisant l'essentiel des travaux plus volumineux en préparation. Ces articles, ne dépassant pas comme règle dix mille signes typographiques, sont donnés en l'une des trois langues: français, anglais, allemand. Ils embrassent les sciences mathématiques, physiques, naturelles et techniques, reproduisant les résultats de recherches scientifiques actuellement en cours ou à peine achevées qui représentent les plus récentes données de l'investigation scientifique.

Les auteurs ont droit chacun à 25 extraits gratuits.

Les manuscrits doivent être adressés à la Rédaction des «Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS»—Moscou, oulitza Koujbysheva, 8.

15 Juillet

COMPTES RENDUS

(DOKLADY)

DE L'ACADÉMIE DES SCIENCES DE L'URSS

COMITÉ DE RÉDACTION

A. Borissiak, de l'Académie, A. Fersman, de l'Académie, A. Frumkin, de l'Académie,
A. Richter, de l'Académie, S. Wawilow, de l'Académie

NOUVELLE SÉRIE

5-me année

Paraissant tous les dix jours

1937

VOLUME XVI, № 2

TABLE DES MATIÈRES

Pages

MATHÉMATIQUES

V. Stepanov (W. Stepanoff). Démonstration arithmétique d'un théorème de B. Segal 75

PHYSIQUE

A. V. Joffe and **A. F. Joffe,** Member of the Academy. Electronic Semi-Conductors in Strong Electric Fields 77
— Properties of the Blocking Layer of Solid Rectifiers 81
H. Mandel und **P. Kutejnikov.** Zur Elektrodynamik der materiellen Medien 83

CHIMIE

N. S Kurnakov, Mitglied der Akademie, **A. V. Nikolaev** und **A. G. Čeliščeva.** Erhitzungskurven der Borate. I 87
— Spezifisches Gewicht und Härte der natürlichen Borate und ihrer Erhitzungsprodukte. II 90
— Hydratationswärme und exothermische Boratumwandlung für Inyoit. Einige Vorstellungen über die Boratumwandlung. III 92
V. V. Čelincev, Corresponding Member of the Academy. Explanation of the Disposition and Inclination of Rows of Molecules in Layers of Organic Acids according to Roentgenograms 95
B. P. Nikolskij and **V. M. Vdovenko.** On the Potential Difference between Solid Silver Halogenides and Aqueous Solutions 99

A. G. Kogan et **V. I. Nikolaev.** Étude sur la polytherme du système binaire HNO_3—HCl et du système ternaire HNO_3—HCl—H_2O 103
N. A. Orlov und **I. S. Mustafin.** Die Oxydation als ein Weg zur Bildung kohlehydratischer Substanzen 107

GÉOLOGIE

V. A. Špak. Une nouvelle méthode de différencier les roches du sondage à l'aide du compteur des gamma-impulsions 109
N. P. Luppov. On the Age of the «Upper Siderite Clays» of the Basin of the River Kuban (North Caucasus) 113
O. S. Vialov. On the Mesozoides of Asia 117
J. A. Efremov. On Stratigraphic Subdivision of the Continental Permian and Jurassic of the USSR on the Basis of the Fauna of Early Tetrapoda 121

ZOOLOGIE

V. I. Calkin. On the Distribution of the Common Dolphin (*D. delphis* L.) in the Black Sea 127

Rédacteur en chef A. Fersman. Rédacteur S. Bernstein.

En composition 19/VI 1937. En impression 22/VII 1937. Nombre de feuilles d'imprimerie 3 1/2. Nombre de caractères par feuille imprimée 65.000. Pages 73—128. Format du papier 72×110 cm. Tirage 1300. Moscou. Glavlit B—15330. Numéro d'édition 737. Numéro typographique 1061.

Imprimerie № 16. Moscou, Trekhproudnyi péréoulok, 9.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

MATHÉMATIQES

DÉMONSTRATION ARITHMÉTIQUE D'UN THÉORÈME DE B. SEGAL

Par STEPANOV (W. STEPANOFF)

(Présenté par I. M. Vinogradow, de l'Académie, le 31. V. 1937)

Dans une note (1) B. Segal applique une formule asymptotique obtenue au moyen d'une méthode analytique, pour démontrer entre autres le théorème suivant:

Étant donné un nombre $N>1$, on peut définir deux entiers positifs $x(N)$, $y(N)$, tels que $N-xy=O(N^{1/4})$, $x\sim y$.

Le but de la présente note est de donner une démonstration arithmétique de ce théorème, démonstration qui fournit d'ailleurs une borne exacte (atteinte pour une infinité de valeurs de N) pour les nombres:

$$d=|N-xy|, \quad \delta=|x-y|.$$

Dans la suite x, y, z, k, l désignent des entiers positifs.

Soit $N\geqslant 1$. Si N est un carré parfait, $N=z^2$, posons $x=y=z$, donc $d=0$, $\delta=0$. Ainsi nous supposerons:

$$z^2<N<(z+1)^2. \tag{1}$$

Si $N=z(z+1)$, on a $x=z$, $y=z+1$; $d=0$, $\delta=1$.

Examinons les deux cas qui restent:

$$\text{I.}\quad z(z+1)<N<(z+1)^2. \tag{2}$$

Formons une suite de nombres:

$$L_0=(z+1)^2,\ L_1=L_0-1=z(z+2),\ \ldots,\ L_{l-1}=L_0-(l-1)^2=$$
$$=(z-l+2)(z+l)>z(z+1)=L^*,$$
$$L_l=L_0-l^2=(z-l+1)(z+l+1)\leqslant z(z+1).$$

La plus grande différence possible entre deux termes consécutifs de la suite

$$L_0,\ L_1,\ \ldots,\ L_{l-1},\ L^* \tag{3}$$

est égale à $L_{l-1}-L_l=2l-1$; elle est atteinte si l'on a $L^*=L_l$ c'est-à-dire, si $z+1=l^2$; la plus grande différence entre les deux facteurs d'un même terme de la suite (3) est

$$(z+l)-(z-l+2)=2(l-1).$$

Si nous désignons un des termes de la suite (3) par xy, nous obtenons:

$$d \leqslant l - \frac{1}{2}, \quad \delta \leqslant 2(l-1).$$

Il ne reste qu'à évaluer l au moyen de N.

D'après la définition de l nous avons:

$$(l-1)^2 < L_0 - z(z+1) = z+1, \quad l^2 \geqslant z+1,$$

par conséquent,

$$\sqrt{z+1} \leqslant l < \sqrt{z+1} + 1, \quad l = [\sqrt{z+1}].$$

En vertu de (1), nous avons:

$$z+1 = [N^{1/4}] + 1, \text{ donc } \quad l \leqslant [N^{1/4}] + 1.$$

Ainsi dans le cas I on a:

$$d \leqslant [N^{1/4}] + \frac{1}{2}, \quad \delta \leqslant 2[N^{1/4}]. \tag{4}$$

Les deux égalités sont vérifiées pour

$$N = l^2(l^2-1) + l + \frac{1}{2}.$$

II. $$z^2 < N < z(z+1). \tag{5}$$

Formons la suite:

$$K_0 = z(z+1), \quad K_1 = K_0 - 2 = (z-1)(z+2), \ \ldots,$$
$$K_{k-1} = K_0 - k(k-1) = (z-k+1)(z+k) > z^2 = K^*,$$
$$K_k = K_0 - k(k+1) = (z-k)(z+k+1) \leqslant z^2.$$

Dans la suite

$$K_0, \quad K_1, \ \ldots, \ K_{k-1}, \quad K^* \tag{6}$$

la plus grande différence de deux termes successifs ne surpasse pas $K_{k-1} - K_k = 2k$. Elle est atteinte, si l' on a $K^* = K_k$, c'est-à-dire si $z = k(k+1)$; la plus grande différence entre les deux facteurs d'un même nombre de la suite (6) est $2k-1$. En désignant l'un des nombres (6) par xy nous obtenons:

$$d \leqslant k, \quad \delta \leqslant 2k-1.$$

Exprimons les bornes de d, δ obtenues, au moyen de N.

D'après la définition de k nous avons:

$$k(k-1) < z, \quad k(k+1) \geqslant z,$$

$$-\frac{1}{2} + \sqrt{z + \frac{1}{4}} \leqslant k < \frac{1}{2} + \sqrt{z + \frac{1}{4}}.$$

On a donc:

$$k = [\sqrt{z}], \quad z = [\sqrt{N}], \quad k = [N^{1/4}].$$

Par suite nous avons dans le cas II:

$$d \leqslant [N^{1/4}], \quad \delta \leqslant 2[N^{1/4}] - 1. \tag{7}$$

Les deux égalités ont lieu pour $N = k^2(k+1)^2 + k$.

Ainsi les bornes exactes pour d et δ sont: (4) pour les intervalles (2), et (7) pour les intervalles (5). Ce résultat ne peut être précisé sans augmenter la borne de δ, les suites (3) et (6) épuisant tous les nombres de l'intervalle (1) pour lesquels la différence de deux facteurs ne surpasse pas $2[N^{1/4}]$.

Institut de Mathématiques,
Université de Moscou.

Manuscrit reçu
le 31. V. 1937.

LITTÉRATURE CITÉE

[1] C. R. Acad. Sci. URSS, III, 95—99 (1934).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

PHYSICS

ELECTRONIC SEMI-CONDUCTORS IN STRONG ELECTRIC FIELDS

By A. V. JOFFE and A. F. JOFFE, Member of the Academy

I. The Problem. A wide use of solid rectifiers and photoelectric cells has aroused in recent years a heightened interest in the properties of semi conductors, and more especially in those of cuprous oxide and selenium as being commonly applied in industry. A detailed theory of electronic semi-conductors has also been developed. This deeper knowledge of semi-conductors has made it possible to reconsider the nature of breakdown and rectification.

Numerous investigations of a great variety of semi-conductors and insulators have shown that in a sufficiently strong electric field Ohm's law is replaced by the so-called Poole's law, an empirical law according to which conductivity is assumed to grow exponentially with the P. D. (potential difference) applied.

From the experimental point of view, the main difficulty of these investigations lies in the substitution of potential difference applied for the field strength in Ohm's law. One of us had shown, as early as 1907—1915, that a continued passage of current results in an accumulation of space charges, which causes a re-distribution of the field within the dielectric. The formation of space charges, especially in electronic cuprous oxide, has been found and investigated by Nasledov and Nemenow. Of still greater importance is the re-distribution of the potential due to chemical heterogeneity. Failure to make due allowance for these factors has often resulted in erroneous statements being made with regard to the interrelations of Ohm's and Poole's laws. Our experiments supply a definite answer to this question.

In order to account for the increase of conductivity in strong fields, the following explanations have been suggested:

1. Ionization by free charges, which had accumulated in the electric field the necessary energy. In 1926, one of us suggested that disruption was due to an ionic avalanche. Nernst and later Hippel investigated the electronic avalanche. Finally, Frenkel and Fröhlich consider the accumulation of energy in the field as a process taking place in spite of repeated diffusion in various directions. The same kind of phenomenon may be inferred from Landau's theory.

The main objection to all these theories lies in the fact that breakdown voltage and currents before disruption do not depend on thickness up to a thickness of $5 \cdot 10^{-5}$ cm (A. P. Alexandrov and A.F. Joffe) and even to $4 \cdot 10^{-6}$ cm (Just, Güntherschultze). Another objection is that, in very thin layers, an increase of conductivity becomes noticeable at P. D.'s of the order of tenths of a volt, which are obviously insulfficient for ionization. Our experiments described below do not confirm any such theory of ionization by collision.

2. Frenkel, Schottky and Waibel have suggested that the increase in conductivity is due not to an increase in the number of charges but to an increase in their mobility. We shall show that this explanation is also in contradiction with experimental data.

3. Zenner explains the increase in conductivity by the percolation of electrons from the metal cathode into the energy zone of conductivity of the semi-conductor. This mechanism of the increase in conductivity is the most natural one from the modern point of view. Still, the conception of rectification deducible from our experiments is in direct contradiction with what Zenner assumes to be the part played by the metal cathode.

4. F. F. Wolkenstein suggested that the increase in conductivity was due to the drawing together of the limits of the normal and the excited electronic levels produced by the electric field (a Stark effect in a solid body). A more conservative estimate than that adopted by Wolkenstein would lead to a much higher value than those experimentally obtained.

Our experiments could be conciliated with such conceptions. Only the dependence of the effect on temperature is in contradiction with them.

II. Method of Measurements. The experiments briefly described below were made on artificially prepared cuprous oxide plates. Over 50 specimens of varying thermal treatment and of a varying percentage of excess oxygen (or deficiency of copper) were examined. In addition to this, we had three monocrystals of cuprite and also plates of ZnO, ZnS, V_2O_5, WO_3, MoS_2, Se, etc. The plates had been furnished (by sublimation of gold in vacuo) with safety-ring electrodes. In order to avoid an accumulation of space charges and the Joule effect, the pressure was switched on for 0.1 sec., the current being measured during 0.001 sec. (or, more precisely, 0.0009 sec.) after switching on. Some sets of measurements, however, were made at 0.02 sec., and others for a steady current measured by a compensation method.

The current was measured either with a string electrometer according to capacity charge, or with a ballistic galvanometer. Voltage was obtained either from a storage battery (up to 800 V), or (up to 6 000 V) from a high capacity (5 μF) rectifying transformer unit. The field strength in the specimen was as high as 80 000 V cm, the average error of observation being 5% with rapid switching on, and 1% with prolonged exposure.

Temperature was measured with a thermoelectric cell soldered to the table to which the specimen was secured. The measurements were made at room temperature, at 0, —20, —80,—180′, and at intermediate temperatures.

III. Darkness Currents At low potential differences (0.1—1000 V/cm), Ohm's law was usually justified in the cuprous oxide within errors of measurement, both for the initial moment and for longer exposures (unless there were inhomogeneities or space charges detected by the discharge current upon switching off potential difference).

So long as the field is weak enough, it cannot naturally disturb the equilibrium concentration of the electrons, the statistic distribution of their velocities, and, consequently, their mobility. Ohm's law may therefore be regarded as a result of thermodynamic equilibrium in the semi-conductor.

It is easy to understand that, in stronger fields, the accumulation of energy at one or several lengths of free path will cause the average speed of the electrons to exceed thermal velocities, which must result in a lowering of mobility and conductivity. The effect produced may become noticeable at thousands of volts per centimetre. It is also clear that in such fields which have the time to bring the electrons out of the thickness of the semi conductor before they have had the time to recombine (or to become secured on the irregularities of the lattice), equilibrium will be disturbed, and Ohm's

law will not apply. None of these phenomena can, however, explain the observed exponential growth of conductivity.

In our experiments, at certain average field strength, $\overline{E} = \frac{V}{d}$, conductivity σ began to rise sharply in conformity with Poole's law. In plotting $\log \sigma$ as a function of $\overline{E}$, we obtained a straight horizontal line for the initial portion (Ohm's law), and an inclined straight line (Poole's law) for the rest (Fig. 1).

The value of E_k varied widely in different cases. The highest observable value of E_k was 30 000 V/cm.

As a rule $E_k \approx 10\,000$ V/cm (this value is in good agreement with Waibel's data, who obtained $E_k \approx 15\,000$ V/cm). In a good many instances, however, E_k fell to 1 000 V/cm, or even to tenths of volts per centimetre. The main cause of this discrepancy probably lies in the fact that our method of measurement only gave the average field in the specimen, but did not give the true field in every portion of the semi-conductor. It is, however, evident that, in case of heterogeneity, a deviation from Ohm's law will begin in that portion of the specimen where the potential gradient is the highest. Any heterogeneity therefore results in a seeming lowering of E_k. In the rectifiers where the non-conducting layer has a thickness of the order of $2 \cdot 10^{-6}$ cm, the departure from Ohm's law begins to be felt at 10^{-2} volts, which gives $\frac{V}{d} \approx 1$ V/cm, whereas $E_k \approx 5\,000$ V/cm.

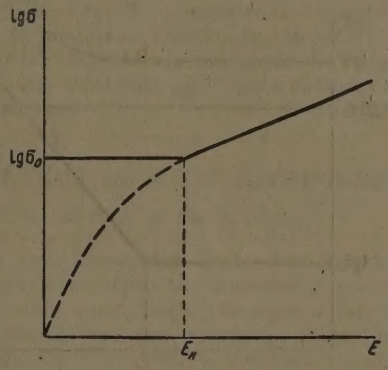


Fig. 1.

In some specimens, the horizontal portion of the curve was replaced, even for the smallest fields of the order of 100 V/cm by a sharper rise of $\log \sigma$ than the one observable after the E_k field had been reached (dotted curve, Fig. 1). This experiment was carried out at liquid air temperature, when the conductivity increased by the field takes many hours to resume its former value. It was to be expected that the thin layer wherein the E_k field had been first reached and which was responsible for the sharp rise of $\log \sigma$, would preserve its high conductivity also in weak fields. On passing from the higher to the lower values of E the sharp initial rise was indeed blotted out, being replaced by the usual course of the curve, as represented by a full line.

Thus, in spite of various discrepancies, we consider the trend of the curve represented in Fig. 1 by a full line to be typical of a homogeneous semi-conductor. The incline of the straight line in the $E_k E$ portion is greatly dependent on temperature. At -180°C, conductivity increases by 4% with a 10^3 V/cm increase of the field. At a temperature of -80°C, the same change in the field increases σ by 20%, while at room temperature the increase is manyfold. Since, with a rise of temperature, the difference in the conductivity of various portions of the specimen become smaller, the increase in the steepness of the growth of σ with the field cannot be put down to the presence of heterogeneities.

No dependence of the incline of the straight line $\log \sigma = f(E)$ on the thickness of the layer of the semi-conductor has been observed by the writers.

In most cases, fairly good straight lines could be obtained, as shown in Fig. 1. All the theories, however, that connect the growth of σ with the kno-

cking out of n electrons from the electrodes or from their normal levels by the field lead to dependences where $\log n$ is linearly dependent on $\frac{1}{E}$. On the other hand, given constant mobility n is proportional to the difference $(\sigma - \sigma_0)$. A linear dependence between $\log(\sigma - \sigma_0)$ and $\frac{1}{E}$ was therefore to be expected. In 7 cases out of 10, within a wide range of fields, it has indeed proved possible to represent $\log \sigma = f\left(\frac{1}{E}\right)$ by a straight line. Only in 4 cases out of 10 was $\log(\sigma - \sigma_0)$ expressed linearly through E.

The nature of the dependence of σ on E does not therefore solve the question of the nature of the increase of σ in strong fields.

IV. Photoelectric Current in Strong Fields. The first of the explanations set forth above (ionization by collision) may be verified in the following manner. If new charges are produced by the already existing free electrons, any increase in their initial number must increase as many times the number of secondary ones, i. e. conductivity in a given field must be proportional to σ_0 and in the diagram (Fig. 2) $\log \sigma$, E the new curve *II* should be parallel to the initial curve *I*. Experiment, however, has given the result shown in Fig. 2.

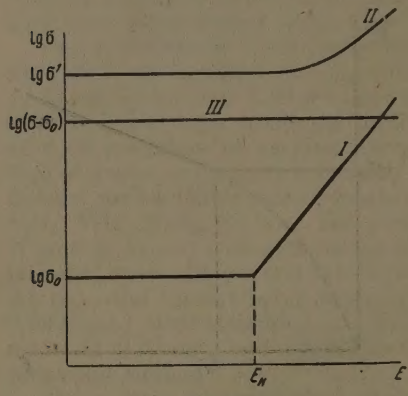


Fig 2.

The number of primary free electrons was increased different numbers of times (from 2 to 100), as compared with darkness equilibrium, by exposure of a photosensitif specimen to light. Only weakly absorbable light had to be used, lest a new heterogeneity should arise. In the same Fig. 2, the horizontal straight line *III* represents the difference between light conductivity and darkness conductivity $[\log(\sigma - \sigma_0)]$.

The additional photo-conductivity due to light has the same value both in fields smaller than E_k and those many times greater than E_k. This experimental fact enables us to draw two conclusions: 1) the increase of conductivity in strong fields does not depend on the number of electrons present, and, consequently, the increase is not due to ionization by collision; 2) mobility in strong fields is the same as in weak fields, so that the second explanation is also wrong.

In a subsequent article dealing with the nature of rectification we shall show that, in spite of Zenner's theory, the increase of σ has no connection with the metal cathode. This invalidates the main portion of the third explanation.

Finally, the fourth explanation is based on the assumption that the width of the energy gap u, which determines conductivity

$$\sigma = \sigma_0 e^{-\frac{u}{2kT}},$$

decreases with the increase of the field. Putting for instance $u = u_0 - \alpha E$, we obtain: $\log \sigma = A + \frac{B}{T} E$.

The nature of the dependence is the same as in Fig. 1, but the dependence of the incline on temperature is at variance with experiment. Whereas expe-

riment shows a several times tenfold increase upon the passage from liquid air temperature to room temperature, the formula provides for a decrease of the incline, reducing it to one-third of its former value.

Thus, none of the four explanations so far suggested is in agreement with the experimental data obtained by the writers.

The only thing that is certain is that the increase of conductivity in strong fields is due to the liberation of electrons by the field, and that the joint action of thermal motion and the field greatly enhances effect.

In cuprous oxide, darkness conductivity consists in the transfer of positive holes. There are some reasons to suppose that part of light conductivity is due to electrons (although this is in contradiction with Engelhardt's direct experiments on the measurement of the Hall effect). If the mechanism of darkness conductivity differs from that of light conductivity, the conclusiveness of the experiments represented in Fig. 2 is somewhat impaired. The properties of semiconductors known to possess an electronic conductivity (ZnO, WO_8) coincide, however, so fully with those of cuprous oxide that there is nothing for it but to assume that both electrons and holes possess one common mechanism of conductivity increase.

PROPERTIES OF THE BLOCKING LAYER OF SOLID RECTIFIERS

By A. V. JOFFE and A. F. JOFFE, Member of the Academy

Solid rectifiers are characterized by two properties: 1) by the increase of conductivity σ_n in the direction of easy flow with the increase in potential difference V and 2) the absence of such an increase, or even a fall in conductivity with the potential difference in the blocking direction. At low voltages of the order of (5—30). 10^{-3} V, Ohm's law holds good, conductivity being independent of the sign of the field.

I. The first of these properties reminds on the results obtained by the writers in studying semi-conductors in strong fields. If the characteristic of the rectifier is expressed in coordinates: $\log \sigma_n = f(V)$, it is a good reproduction of the corresponding curve for a semi-conductor containing a thin layer of lower conductivity (cf. Fig. 1 of foregoing article showing dotted curve). The thikness of the blocking layer of the rectifier has been repeatedly determined from the capacity. It is of the order of $2 \cdot 10^{-6}$ to 10^{-5} cm; appreciable departures from Ohm's law appear at (10—30) 10^{-3} V, which corresponds to a field of 1000—15 000 V/cm. Similar values, and even slightly lower ones, were obtained by the writers for a well degassed cuprous oxide.

Both Jouset's experiments with artificially deposited layers of varying thickness, and Hartman's experiments show that the difference between two currents flowing in opposite directions and the departure of the easy flow current from Ohm's law set in at potenitial differences that are the greater the thicker the non-conducting layer where the potential drop is localized. In expressing the potentials in field strength we obtain the above fairly steady values of the critical field. For mica, however, the field E_k is as high as $2 \cdot 10^5$V/cm, in good agreement with the experimentally found point where departure from Ohm's law begins.

Thus, the properties of the easy flow currents are not only qualitatively, but also quantitatively accounted for by the supposition that in thin blocking layers the same growth of conductivity with the field takes place as in the thicker layers studied by us.

II. The dependence of current on direction has been observed by the writers also in thicker layers of semi-conductors, the following peculiarities being noted:

1. Within the limits of applicability of Ohm's law, no asymmetry of darkness currents with direction has been observed by the writers. Here, the resistance of the specimen is equal to the sum total of the resistances of its separate layers.

2. Asymmetry occurred at the field (Fig. 1) reaching its critical value E_k whenever the specimen had a less conducting layer (same as in rectifiers).

3. In cuprous oxide, with fields stronger than E_k, the current flowing from the more conducting to the less conducting portion was invariably greater than that flowing in the opposite direction (which again is in full agreement with what we observe in rectifiers). The same result was obtained with two separate plates of cuprous oxide of different specific conductivity.

The rectifying properties of cuprous oxide rectifiers can thus also be reduced to phenomena in strong fields.

III. A comparison of Jouset's experiments with those of Hartmann shows that, whatever the nature of the blocking layer (shellac, bakelite, mica, quarz, molybdenum oxide), the easy flow current carries mobile charges from the semi-conductor to the boundary of the blocking layer. When the mechanism of the current consists in transferring positive holes (cuprous oxide, selenium), the easy flow current flows from the semi-conductor to the insulator. If however, the current is carried by electrons (zinc oxide, aluminum oxide) the easy flow current flows in the opposite direction. In that case, the boundary between the metal and the insulator is of no special importance; any insulator and any metal may be used. The sign of the rectification is determined solely by the mechanism of the current in the semi-conductor.

It is interesting to note that, while producing in the cuprous oxide a heterogeneous specific conductivity by exposing one side of the plate to strongly absorbable light, we also obtained an asymmetry of the current. As, however, in this case, the mobile charges were the electrons which had been transferred by the light into the zone of free levels, a stronger current was obtained when the electrons were transferred from a more conducting layer to a less conducting one, i. e. when the illuminated electrode was the cathode.

IV. What is then the mechanism of the current in the blocking direction? Here, the mobile charge carriers move away from the boundary of the insulator, where the field lies beyond the limits of applicability of Ohm's law. The thermal movement fails to make up the loss of charge, and near the boundary a space charge is formed of a sign opposite to that of the current carriers in the semi-conductor. This charge lowers the field in the semi-conductor. In industrially applied rectifiers, it also increases the thickness of the low conductivity layer of the rectifier, as shown by capacity measurements at different potentials in the blocking direction.

A great variety of phenomena observable in industrial rectifiers find an adequate explanation from the point of view set forth here. The latter agrees on the whole with the statement of Losev and Waibel to the effect that the rectification sign is determined by resistivity gradient; and the currents, by concentration of strong electric fields in the blocking layer.

It would thus appear imperative to discard: 1) the hypothesis of a gap permeable to electrons (A. F. Joffe and J. I. Frenkel); 2) the explanation based on the assumption that some of the electrons cover distances exceeding the average length of the path (A. F. Joffe and J. I. Frenkel); 3) the hypothesis of emission from cold metals in electric fields (van Geel). The theory of currents before breakdown involving the percolation of electrons from the metal cathode (Zenner) also requires important modifications.

Physico-Technical Institute.
Leningrad

Received
26. V. 1937.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

PHYSIK

ZUR ELEKTRODYNAMIK DER MATERIELLEN MEDIEN

Von H. MANDEL und P. KUTEJNIKOV

(Vorgelegt von S. I. Wawilow, Miiglied der Akademie, d. 11. VI. 1937)

Die elektromagnetischen Vektoren ordnen wir nach Minkowski in zwei Vierertensoren $F^{ik} = -F^{ki}$ und $H^{ik} = -H^{ki}$ folgendermassen zusammen:

$$\mathfrak{E} \to (F^{41}, F^{42}, F^{43}); \quad \mathfrak{B} \to (F^{23}, F^{31}, F^{12});$$
$$\mathfrak{D} \to (H^{41}, H^{42}, H^{43}); \quad \mathfrak{H} \to (H^{23}, H^{31}, H^{12}).$$

Die allgemeinste lineare Beziehung zwischen H^{ik} und B^{ik} wird durch einen Tensor vierten Ranges S^{iklm} mit der Symmetrieeigenschaft:

$$S^{iklm} = -S^{ikml} = -S^{kilm}, \tag{1}$$

gegeben:

$$H^{ik} = S^{ik}{}_{\alpha\beta} F^{\alpha\beta}. \tag{2}$$

Der Tensor S^{iklm} wurde von I. Tamm* für den Fall anisotroper Medien studiert, wobei sich noch die Symmetrieeigenschaft

$$S^{iklm} = S^{lmik}$$

erwies, die der Symmetrie der gewöhnlichen dreidimensionalen ε^{ik} und $(\mu^{-1})^{ik}$ entspricht. Wir können aber ohne weiteres auch den allgemeineren Fall der Hermiteschen Symmetrie der komplexen $\varepsilon^{ik} = \overline{\varepsilon^{ki}}$, $(\mu^{-1})^{ik} = \overline{(\mu^{-1})^{ki}}$** für anisotrop-gyrotrope Medien*** mit in Betracht ziehen, indem wir statt dessen

$$S^{iklm} = \overline{S^{lmik}} \tag{3}$$

setzen.

Durch den Vergleich der vierdimensionalen Formel (2) im Ruhesystem mit den entsprechenden dreidimensionalen Formeln könnte man sich den physikalischen Sinn der einzelnen Komponenten von S^{iklm} klar machen.

Nun sind wir aber im Stande (und dies ist der nichttriviale Resultat unserer Betrachtung)—unter Einfürung der Vierergeschwindigkeit V^i

---

* Russisch: Ит. Тамм, ЖРФ-ХО, VI, 248 (1924). In der deutschen Sprache findet man dies, z. B. bei J. Frenkel, Lehrbuch der Elektrodynamik, Bd. II, Berlin, 1928.

** Der Strich bedeutet das Komplex-Konjugierte.

*** Eingehende Untersuchung der Verallgemeinerung der relativistischen makroskopischen Beziehungen für komplexe Grössen findet man in der Dissertation von P. Kuteinikov (Leningrad, 1935).

des Mediums—den Tensor vierten Ranges S^{iklm} im allgemeinsten Falle durch zwei (den ε^{ik} und $(\mu^{-1})^{ik}$ entsprechenden) Vierertensoren zweiten Ranges und B^{ik} A^{ik} in einer invarianten Weise folgendermassen auszudrücken:

$$S^{iklm} = \frac{1}{2}\left\{A^{im}V^kV^l + A^{kl}V^iV^m - A^{il}V^kV^m - A^{km}V^iV^l + \right.$$
$$\left. + E^{ikos}E^{lm\beta\tau}V_\sigma V_\tau B_{\alpha\beta}\right\} \qquad (4)$$

(E^{iklm} — Tensor von Levi-Civita).

Die Tensoren A^{ik} und B^{ik} müssen Hermitesch sein:

$$A^{ik} = \overline{A^{ki}}; \quad B^{ik} = \overline{B^{ki}}. \qquad (5)$$

Das letzte Glied in (4) genügt den Eigenschaften (1) und (3); man sieht, dass die übrigen vier zusammen eine Kombination darstellen, die gerade so symmetrisiert ist, um ebenfalls (1) zu genügen.

Im Ruhesystem $\overset{\circ}{K}$ müssen die Komponenten von A^{ik} und B^{ik} ($i, k = 1, 2, 3$) einfach die Komponenten der dreidimensionalen Tensoren ε^{ik} und $(\mu^{-1})^{ik}$ darstellen:

$$\overset{\circ}{A}{}^{ik} = \overset{\circ}{\varepsilon}{}^{ik}; \quad \overset{\circ}{B}{}^{ik} = (\overset{\circ}{\mu}{}^{-1})^{ik} \qquad (i, k = 1, 2, 3)$$

und die übrigen Komponenten sind willkürlich zu wählen.

Am einfachsten liegen die Verhältnisse beim gewöhnlichen isotropen Medium (ohne Gyration); in diesem Falle hat man einfach zu setzen

$$A^{ik} = \varepsilon G^{ik}; \quad B^{ik} = \frac{1}{\mu}G^{ik}, \qquad (6)$$

wo ε und $\frac{1}{\mu}$ vierdimensionale Skalare darstellen. Für den leeren Raum ist folglich

$$A^{ik} = B^{ik} = G^{ik}$$

(G^{ik} — Fundamentaltensor), und

$$S^{iklm} = \frac{1}{2}(G^{il}G^{km} - G^{im}G^{kl}). \qquad (7$$

Multiplizieren wir (2) skalar mit V_k:

$$V_\gamma H^{i\gamma} = V_\gamma S^{i\gamma}{}_{\alpha\beta}F^{\alpha\beta}, \qquad (8)$$

wobei man erhält (wegen $V^\gamma V_\gamma = -1$):

$$V_\gamma S^{i\gamma lm} = \frac{1}{2}\left\{(A^{il} + A^{\gamma l}V^iV_\gamma)V^m - (A^{im} + A^{\gamma m}V^iV_\gamma)V^l\right\}. \qquad (9)$$

Nach dem Einsetzen von (9) in (8) und Addieren von

$$(A^{i\gamma}V^lV_\gamma + A^{\gamma\alpha}V^iV^lV_\gamma V_\alpha)V^mF_{lm} = 0$$

folgt

$$V_\gamma H^{i\gamma} = \mathfrak{A}^i_\alpha V_\beta F^{\alpha\beta} \qquad (10)$$

mit

$$\mathfrak{A}^i_\alpha = A^i_\alpha + A^\gamma_\alpha V^iV_\gamma + A^i_\gamma V_\alpha V^\gamma + A^\gamma_\sigma V^iV_\alpha V_\gamma V^\sigma. \qquad (11)$$

Multipliziert man nun (2) skalar mit $V^\gamma E_{i\gamma ik}$ und wertet man ebenso den Produkt $V^\gamma E_{i\gamma\alpha\beta}S^{\alpha\beta lm}$ aus:

$$V^\gamma E_{i\gamma\alpha\beta}S^{\alpha\beta lm} = -E^{lm\sigma\tau}(B_{i\sigma} + B_{\gamma\sigma}V_iV^\gamma + $$
$$+ B_{i\gamma}V_\sigma V^\gamma + B_{\gamma\rho}V_\sigma V_iV^\gamma V^\rho)V_\tau, \qquad (12)$$

so erhält man:

$$V^\gamma E_{i\gamma\alpha\beta} H^{\alpha\beta} = \mathfrak{B}_i^\sigma E_{\sigma\tau\alpha\beta} V^\tau F^{\alpha\beta}, \tag{13}$$

oder mittels Einführung der dualen Feldtensoren H^{*ik} und F^{*ik}

$$V_\gamma H^{*i\gamma} = \mathfrak{B}_\alpha^i V_\beta F^{*\alpha\beta} \tag{14}$$

mit

$$\mathfrak{B}_\alpha^i = B_\alpha^i + B_\alpha^\gamma V^i V_\gamma + B_\gamma^i V_\alpha V^\gamma + B_\sigma^\gamma V^i V_\alpha V_\gamma V^\sigma, \tag{15}$$

Im Ruhesystem $\mathring{K}$ bekommt man aus (11) und (15):

$$\left.\begin{aligned} &\mathring{\mathfrak{A}}^{ik} = \mathring{A}^{ik} = \mathring{\varepsilon}^{ik}; \quad \mathring{\mathfrak{B}}^{ik} = \mathring{B}^{ik} = (\mathring{\mu}^{-1})^{ik} \\ &\mathring{\mathfrak{A}}^{i4} = \mathring{\mathfrak{A}}^{4i} = \mathring{\mathfrak{A}}^{44} = \mathring{\mathfrak{B}}^{i4} = \mathring{\mathfrak{B}}^{4i} = \mathring{\mathfrak{B}}^{44} = 0 \end{aligned}\right\} \quad (i, k = 1, 2, 3) \tag{16}$$

Die Vierertensoren $\mathfrak{A}^{ik}$ und $\mathfrak{B}^{ik}$ stellen Projektionen von A^{ik} und B^{ik} auf den zu V^i senkrechten dreidimensionalen Raum dar.

A^{ik} und B^{ik} können wir nun in (4) durch $\mathfrak{A}^{ik}$ und $\mathfrak{B}^{ik}$ ersetzen, denn die Differenzen $A^{ik} - \mathfrak{A}^{ik}$ und $B^{ik} - \mathfrak{B}^{ik}$ müssen sowieso einfach aus (4) ausfallen.

Beim anisotropen Medium ohne Gyration, wo die Tensoren A^{ik} und B^{ik} symmetrisch sind, können wir im Ruhesystem das Hauptachsensystem, d. h. das vierdimensionale Hauptachsensystem $\mathring{\mathring{K}}$ für $\mathfrak{A}^{ik}$ (bzw. $\mathfrak{B}^{ik}$) einführen*. In jedem solchen Koordinatensystem K', welches aus $\mathring{\mathring{K}}$ durch reine Lorentztransformation (ohne räumliche Drehung) entsteht, fällt (10) mit

$$V'_\gamma H'^{i\gamma} = \mathring{\mathring{\mathfrak{A}}}_\alpha^i V'_\beta F'^{\alpha\beta} \tag{17}$$

zusammen. Unter entsprechenden Definitionen geht (14) ins

$$V'_\gamma H'^{*i\gamma} = \mathring{\mathring{\mathfrak{B}}}_\alpha^i V'_\beta F'^{*\alpha\beta} \tag{18}$$

über.

Im Spezialfall isotroper Medien gehen (17) und (18) in die wohlbekannten Gleichungen von Minkowski über.

Wir sehen also, dass diese Gleichungen [und ihre Verallgemeinerungen (10), (14) für ein anisotrop-gyrotropes Medium] sich leicht als eine unmittelbare Folgerung unserer allgemeinen Formel (4) herleiten lassen.

Das Gesagte gestattet schliesslich den Tensor $\mathfrak{A}^{ik}$ als Vierertensor der Dielektrizitätskonstanten, und $\mathfrak{B}^{ik}$ als Vierertensor der (reziproken) magnetischen Permeabilitätskonstanten zu bezeichnen.

Physikalisches Institut
der Universität Leningrad.

Eingegangen
d. 11. VI. 1937.

* Das Hauptachsensystem kann für $\mathfrak{A}^{ik}$ und für $\mathfrak{B}^{ik}$ verschieden sein; dass Ruhesystem ist durch die obigen Formeln eindeutig bestimmt.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

CHEMIE

ERHITZUNGSKURVEN DER BORATE

Von N. S. KURNAKOV, A. V. NIKOLAEV und A. G. ČELIŠČEVA

Die Entdeckung der Inderschen Borlager erforderte eine eingehende Untersuchung der physikalisch-chemischen Eigenschaften der natürlichen Borate. Ein Teil dieser Arbeit wurde im Institut für allgemeine und anorganische Chemie der Akademie der Wissenschaften der UdSSR ausgeführt. Die Sammelfunde zweier Expeditionen dieses Institutes (in den Jahren 1935 und 1936) ermöglichten eine solche Untersuchung der Mineralien. Vor allen Dingen wurden Erhitzungskurven erhalten, wie sie in der Literatur noch nicht beschrieben sind. Ausser den Inderschen Mineralien (№ 2, 4, 6, 7, 9, 10, 11 d. Tabelle) wurden noch die Mineralien ausländischer Fundstätten (Pandermit aus Panderma und Borazit aus Stassfurt) in den Kreis unserer Untersuchungen mit einbezogen.

Aus Gründen der Vollständigkeit wurden die Erhitzungskurven der synthetischen Produkte Pinnoit und Kaliborit* aufgenommen.

Die Analysen der untersuchten Stoffe bringen wir an anderer Stelle. Hier sei nur auf die grosse Reinheit der natürlichen Produtke hingewiesen.

Die Aufnahme der Erhitzungskurven (einfache und Differentialmethode geschah mit dem Pyrometer von Akad. N. S. Kurnakov. Eine gleichmässige Erwärmung wurde mit hoher Genauigkeit durch eine automatische Vorrichtung, den sogenannten Kontaktpotenzialregulator, gewährleistet. Dies ist aus dem nahen Neigungswinkel der weiter unten angeführten Kurven zu ersehen. Gleichmässige Erwärmung mit kleiner Geschwindigkeit (ungefähr 2.5° C pro Minute, d. h. bis etwa 900° im Verlauf von 6 Stunden) erleichtert die Ablesung der Erhitzungskurven. Die erhaltenen Kurven besitzen 4 Arten von Haltestellen:

1. Die endothermischen Haltestellen, die mit Wasserabgabe verbunden sind, sind nicht umkehrbar.
2. Die endothermische Haltestelle, die mit dem Polymorphismus (Borazit) verbunden ist, ist umkehrbar.
3. Die endothermische Haltestelle, die offensichtlich mit der Schmelzung (Kaliborit) zusammenhängt, ist umkerhbar.
4. Fie exothermischen Haltestellen, die mit der Umwandlung der Stoffe im festen Zustande verknüpft sind, sind nichtumkehrbar.

Weiter unten führen wir die Haltestellen-Temperaturen der untersuchten Stoffe an.

* Beide Produkte wurden von uns nach der Methode von Van't Hoff synthetisiert (siehe «Ozeanische Salzablagerungen», S. 183 und 186; russiche Übersetzung von A. V. Nikolajev, 1936).

Haltestellen-Temperaturen (°C) der Erhitzungskurven der Borate

№	Mineral	Endotherm. Haltestellen				Exotherm. Haltestellen	
		I	II	III	IV	I	II
		A.—E.				A.—E.	
1	Pinnoit (synth.) ($MgO \cdot B_2O_3 \cdot 3H_2O$)	290—326	—	—	—	730—760	800
2	Ascharit ($MgHBO_3$)	615—680	—	—	—	—	—
3	Borazit ($6MgO \cdot 8B_2O_3 \cdot MgCl_2$)	350*	—	—	—	—	—
4	Kolemanit ($2CaO \cdot 3B_2O_3 \cdot 5H_2O$)	350—390	410	—	—	710—770	—
5	Pandermit (aus Panderma) ($8CaO \cdot 10B_2O_3 \cdot 15H_2O$)	225—355	455	—	—	770—910	—
6	Pandermit (Indersalzsee) ($8CaO \cdot 10B_2O_3 \cdot 15H_2O$)	270	405	—	—	840	—
7	Inyoit ($2CaO \cdot 3B_2O_3 \cdot 13H_2O$)	110	115	470	730	860—1080	—
8	Kaliborit (synth.) ($K_2O \cdot 4MgO \cdot 11B_2O_3 \cdot 18H_2O$)	275	750	815*	—	625—675	—
9	Boronatrokalzit ($Na_2O \cdot 2CaO \cdot 5B_2O_3 \cdot 16H_2O$)	150—200	—	—	—	615—770	—
10	Hydroborazit [$CaO \cdot MgO \cdot 3B_2O_3 \cdot 6H_2O$]	314	—	—	—	780	810—890
11	Inderit**[$2MgO \cdot 3B_2O_3 \cdot 15H_2O$]	135	—	—	—	780	—

Alle endothermischen Haltestellen, die mit Wasserabgabe verbunden sind, liegen unter 455°. Ascharit—ein Magnesiumsalz der Orthoborsäure ($MgHBO_3$)—bildet eine Ausnahme: es verliert das Konstitutionswasser bei ungefähr 600°. Kolemanit, das bei 350° die Hauptmasse seines Wassers abgibt, d. h. in der Nähe der kritischen Temperatur des Wassers, führt bei gleichzeitiger Volumenvergrösserung Mineralteilchen weg (raucht), und daher ist für ihn die Wasserbestimmung mit der gewöhnlichen Methode unmöglich. Nach dem Charakter der Haltestellen zu urteilen, kann man nur in einem Falle völlig sicher den zeolithen Charakter des Wassers feststellen. Beim Pandermit sind die Haltestellen ausserordentlich verwaschen (Fig. 1). Zu dem gleichen Ergebnis kamen auf Grund der Entwässerungskurven des Pandermits A. Gutbier, Q. Huttig und G. Linck (1).

Für alle übrigen Mineralien sind die Haltestellen scharf, und für Inyoit z. B. kann man 3 Haltestellen angeben, die mit dem Wasser verknüpft sind. Berücksichtigen wir noch die ausgezeichnete Übereinstimmung der Analysenresultate mit den theoretischen Formeln für die Mineralien der verschiedenen Fundstätten, so haben wir vorläufig noch keine Grundlagen dafür, den zeolithen Charakter des Wassers bei allen untersuchten Boraten, mit Ausnahme

* Diese Haltestelle ist umkehrbar.

** Das Mineral ist von A. M. Boldyreva (Zentral-Institut für geologische Forschung) entdeckt worden. Die Analyse, die von uns ausgeführt wurde, ergab ein Resultat, das der Formel $2MgO \cdot 3B_2O_3 \cdot 15H_2O$ entsprach.

Analyse	Theorie
$\frac{B_2O_3}{RO} = 1.49$	$\frac{B_2O_3}{RO} = 1.50$
$B_2O_3 = 36.65\%$	$B_2O_3 = 37.32\%$
$H_2O = 48.42\%$	$H_2O = 48.27\%$
$CaO = 0.57\%$	—
$MgO = 14.71\%$	$MgO = 14.41\%$

des Pandermits, anzunehmen. Beachtung verdient die Bindungsfestigkeit des Wassers im Innern der Boratmoleküle (siehe Tabelle I).

Die exothermischen Haltestellen sind von bedeutendem Interesse. Sie sind mit Ausnahme des Ascharits und Borazits bei allen Boraten beobachtet worden.

Wie die wiederholten Erhitzungskurven für Kaliborit (2 Kurven), ebenso die Abkühlungskurven für Injoit, Boronatrokalzit (2 Kurven), Hydroborazit (2 Kurven) und Pandermit gezeigt haben, sind diese Haltestellen nichtumkehrbar. Der exothermische Effekt und die Geschwindigkeit des Prozesses sind so gross, dass eine Reihe von Boraten sich selbst um 150—200° mehr als die Temperatur des Ofenraums erwärmt. Für Pinnoit und Hydroborazit sind 2 exothermische Haltestellen zu vermerken. Die exothermische Umwandlung wird begleitet von einem Zusammenbacken der Boratpulver zu einer sehr festen, kompakten Masse. Indem wir ihr Charakteristikum in Betracht ziehen, machen wir den Vorschlag, sie mit Boratumwandlung (Boratumstelle) zu bezeichnen.

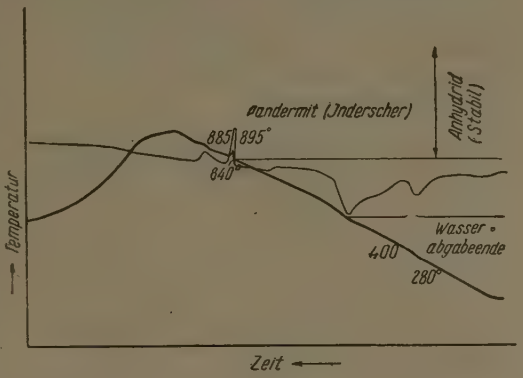


Abb. 1.

Interessante Resultate ergibt ein Vergleich der Erhitzungskurven der Borate nach Gruppen.

Kalziumborate. Das Inyoit (Fig. 2) hat, nach der Differentialkurve zu urteilen, 4 Haltestellen mit Wärmeabsorption. Daher kann es sehr leicht von Pandermit (2 Haltestellen) und Kolemanit (1 Haltest.) unterschieden werden. Kolemanit hat zum Unterschied gegen Pandermit und Inyoit einen verhältnismässig kleinen Wärmeeffekt der exothermischen Umwandlung. Die charakteristischen, «verwaschenen» Haltestellen des Pandermits sondern ihn scharf von den anderen Kalziummineralien ab.

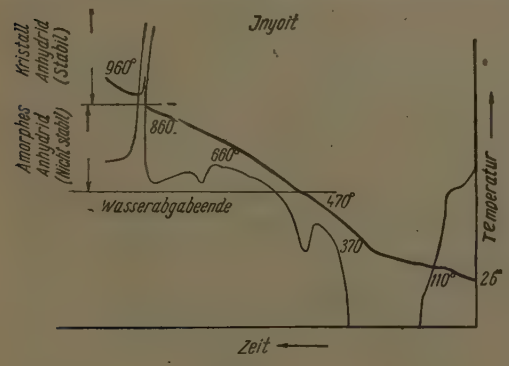


Abb. 2.

Magnesiumborate. Für Borazit liegt die umkehrbare endothermische Haltestelle bei ungefähr 350° (Polymorhismus (2)) und ist das Fehlen der exothermischen Umwandlung charakteristisch. Letztere wurde auch beim Ascharit nicht gefunden, dessen sehr hoch gelegene endothermische Haltestelle (bei ungefähr 650°) mit der Abgabe des Konstitutionswassers verbunden ist*. Pinnoit besitzt zwei exothermische Umwandlungen und eine nichtumkehrbare endothermische bei ungefähr 325°.

* Nach der Erhitzung ist in 1/10 HCl leicht lösbar; um die Überführung des Ascharits in Lösung bei seiner Bearbeitung zu erleichtern, empfiehlt es sich ihn zu erhitzen.

Die Doppelborate sind ebenso leicht an ihren Erhitzungskurven zu erkennen. Kaliborit — an der umkehrbaren endothermischen Haltestelle. Sie liegt nach der exothermischen Umwandlung, die, beiläufig bemerkt, bei der tiefsten Temperatur stattfindet. Hydroborazit zeichnet sich durch zwei exothermische Haltestellen aus (siehe Pinnoit). Boronatrokalzit, der viel Wasser enthält, ist charakteristisch durch die niedrige Temperatur seiner endothermischen Haltestelle.

Die Erhitzungskurven bei den Boraten sind so individuell, dass man aus denselben die Mineralien bestimmen kann. Von diesem Standpunkt aus gestatten die tief gelegene endothermische Haltestelle beim Inderit (140°) und eine sehr kleine exothermische, ihn als selbständiges Mineral (Übergang zum Ascharit) anzusehen.

Institut für allgemeine und anorganische Chemie.
Akademie der Wissenschaften der UdSSR.
Moskau.

Eingegangen
d. 29. IV. 1937.

ZITIERTE LITERATUR

[1] A. Gutbier, G. Huttig u. G. Linck, ZS. f. Elektrochem., 32, 79 (1929).
[2] P. Groth. Einführung in die chemische Kristallographie. Übersetzung aus dem Deutschen, S. 8., Odessa 1911.

SPEZIFISCHES GEWICHT UND HÄRTE DER NATÜRLICHEN BORATE UND IHRER ERHITZUNGSPRODUKTE. II

Von N. S. KURNAKOV, Mitglied der Akademie, A. V. NIKOLAEV und A. G. ČELIŠČEVA

In unserer vorhergehenden Mitteilung («Erhitzungskurven der Borate») wurde darauf hingewiesen, dass die von neuem aufgefundene exothermische Boratumwandlung von einem Zusammenbacken und einer Härtezunahme begleitet wird. In der vorliegenden Mitteilung werden die Ergebnisse der Bestimmung des spezifischen Gewichts und der Härte der natürlichen Borate und ihrer Erwärmungsprodukte angeführt: 1) nach der Entwässerung, b) nach der Boratumwandlung.

Das spezifische Gewicht wurde bei 25° in Pyknometern bei Entfernung der Luft, im Vakuum, bestimmt. Als Flüssigkeit wurde destilliertes Toluol verwendet. Die Härte wurde nach der Moosschen Skala bestimmt.

Die von uns erhaltenen spezifischen Gewichte der natürlichen Stoffe unterscheiden sich wenig von den Literaturangaben für die Mineralien der ausländischen Fundstätten (siehe 3. Spalte der Tab. 1). Die Borate, die bei Temperaturen unterhalb der exothermischen Boratumwandlung (Tab. 1, 4. Spalte) entwässert wurden, gaben in 4 Fällen ein kleineres spezifisches Gewicht als bei dem natürlichen hydratierten Produkt. (s. IV, V, VII, VIII, IX, X der Tab. 1).

Gewöhnlich wird die Wasserabgabe von einer Zunahme des spezifischen Gewichtes begleitet. Dies ist der Fall für die meisten Hydrate der Salze.

Wenn wir annehmen, dass bei Entwässerung das Boratmolekül in Oxyde zerfällt, so kann man für diesen Fall das spezifische Gewicht theoretisch berechnen (Tab. 1, 6. Spalte). Wie für 4 Fälle zu sehen ist (I, IV, V und X), erwies sich nach der Entwässerung das spezifische Gewicht sogar kleiner, als bei dem mechanischen Gemisch der entsprechenden Oxyde. Dies alles

Tabelle 1

Spezifisches Gewicht und Härte der Borate

№	Mineral	Spez. Gew. des Minerals		Spez. Gew. d. entwässerten Produktes	Spez. Gew. nach d. Boratumwandlung	Berechn. spez. Gew.	Kontraktions-Koeffizient	Härte	
		Unsere Bestimmung	Nach Literaturangaben					des natürl. Produktes	nach der Umwandlung
	1	2	3	4	5	6	7	8	9
I	Inyoit	1.88	1.87	1.91	2.62	2.13	1.78	2.5	6.5
II	Boronatrokalzyt . .	1.98	1.65	2.22	2.60	2.05	1.73	1.0	3.5
III	Kaliborit (synth.) . .	2.08	2.13	2.14	2.18	2.00	1.38	—	4.5
IV	Pinnoit (synth.) . . .	2.28	2.3—3.4	1.91	2.67	2.19	2.24	Pulver	
V	Hydroborazit	2.18	2.0	1.99	2.55	2.11	1.23	2.5	5.0
VI	Ascharit	2.71* 2.70	2.7	2.84	—	2.45	1.17	4.0	—
VII	Pandermit (Panderma)	2.49	2.3—2.5	—	2.55	2.19	1.13	2.5	6.0
VIII	Pandermit (28. Fundstätte Inder) . . .	2.47	—	2.27 2.26	2.63	2.19	1.13	Zerfällt in Pulver	5.5
IX	Dasselbe (6. Fundstätte Inder) . . .	2.48	—	2.34	2.64 2.65	2.19	1.13		5.5**
X	Kolemanit	2.38	2.42	1.94 1.95	2.39 2.41	2.13	1.05	4.5	5.0

führt zu der Ansicht, dass bei der Dehydratierung tiefgehende Veränderungen im Kristallgitter*** vor sich gegangen sind.

In dieser Hinsicht interessante Resultate gab der Kontraktionskoeffizient, der in Tab. 1, 7. Spalte, angeführt ist. Zur Bestimmung desselben gingen wir von einem Grammol des hydratischen Produktes aus und berechneten das spezifische Gewicht des entwässerten Stoffes unter der Annahme, dass trotz des Wasserverlustes das Volumen des Grammols nicht abnimmt. Durch diese Grösse wurde dann das experimentell erhaltene spezifische Gewicht des entwässerten Produktes dividiert, und das Resultat ist der Kontraktionskoeffizient. Wie aus Tab.1 (7. Spalte) ersichtlich ist, erreicht der Kontraktionskoeffizient die Maximalwerte für Inyoit und Boronatrokalzit, für welche der Hydratcharakter des Wassers unbezweifelbar ist, und die kleinsten Werte für Pandermit und Kolemanit. Die letzteren haben auch nach anderen Untersuchungen Zeolithwasser****. Bemerkenswert ist, dass die Befreiung von 5 und 7.5 Wassermolekülen von einer Verringerung des spezifischen Gewichts begleitet wird, während die absolute Kontraktion im ganzen 5—13% beträgt. Es ist von Interesse, hier die Daten von I. W. Mellor und A. D. Holdcroft([1]) über den chinesischen Ton und Kaolinit nach der Entwässerung und der exothermischen Koalinitumwandlung (1050°C) anzuführen.

---

* Die harte Verschiedenartigkeit des Minerals wurde uns liebenswürdigerweise von M. N. Godlewskij geliefert, wofür wir ihm unseren Dank aussprechen.

** Die Härte des synthetischen Pandermits beträgt nach der Umwandlung auch 5.5.

*** Nach unseren Beobachtungen sind die Wasserverluste beim Inyoit und Kolemanit von einer Trübung begleitet.

**** Siehe die Arbeit derselben Autoren «Erhitzungskurven der Borate».

Tabelle 2

Spezifisches Gewicht des chinesischen Tons (I) und Koalinits (II)

	Nach der Erhitzung bis			Berechnet. spez. Gewicht	Kontraktions-Koeffizient
	110°	900°	1200°		
I	2.615	2.56	2.73	—	1.14
II	2.8	3.525	3.94	3.13	1.57

Aus der Tab. 2 folgt, dass der Zerfall in Oxyde bei der Entwässerung des Koalinits(2) mit den spezifischen Gewichten in Einklang gebracht werden kann, nur unter der Annahme einer teilweisen Dissoziation in Oxyde.

Die exothermische Boratumwandlung wird von einem scharfen Anstieg des spezifischen Gewichtes begleitet: beim Pinnoit wächst es z. B. um 0.73 oder um ungefähr 40%. Die Annäherung der Elemente des kristallischen Gitters wird von einer beträchtlichen Härtezunahme begleitet (siehe Tab. 1), die beim Inyoit 6.5 erreicht. Die Kontraktion muss nach den gegenwärtig herrschenden Vorstellungen von einer Wärmeausscheidung begleitet sein. Hierin kann man die Ursache der exothermischen Umwandlung sehen. Bemerkenswert ist der Unterschied in der Härte und dem spezifischen Gewichte nach der Boratumwandlung für Inyoit und Kolemanit (siehe Tab. 1). Dieser Unterschied ist dadurch bezeichnend, dass die Bruttoformel in beiden Fällen die gleiche ist [$2CaO.3B_2O_3$]. Inyoit hat Hydratwasser, während nach gewissen Angaben Kolemanit Zeolithwasser enthält. Da nun weder Entwässerung noch Umwandlung sie bei der gleichen Zusammensetzung identisch machen können, so haben wir vor uns einen im höchsten Grade lehrreichen Dimorphismus. Es sei bemerkt, dass im gegebenen Fall, sowohl spezifisches Gewicht als Härte für die Stoffe bestimmt wurden, deren Erhitzungskurven aufgenommen wurden. Für jede Probe wurden je 3 Bestimmungen des spezifischen Gewichts vorgenommen. Den gleichen Unterschied nach der exothermischen Umwandlung kann man für das spezifische Gewicht und die Härte unserer Inderschen und des türkischen Pandermite feststellen (siehe Tab. 1). Interessant ist, dass unsere Mineralien der Härte nach das gleiche Produkt wie der synthetische Pandermit gaben, welcher die gleiche Umwandlung durchmachte.

Institut für allgemeine und
anorganische Chemie.
Akademie der Wissenschaften der UdSSR.
Moskau.

Eingegangen
d. 29. IV. 1937.

ZITIERTE LITERATUR

[1] J. W. Mellor a. A. D. Holdcroft, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, VI, 478. [2] G. Tammann u. W. Pape, ZS. f. anorg. u. allg. Chemie, 127, 43—67 (1927).

HYDRATATIONSWÄRME UND EXOTHERMISCHE BORATUMWANDLUNG FÜR INYOIT. EINIGE VORSTELLUNGEN ÜBER DIE BORATUMWANDLUNG

N. S. KURNAKOV, Mitglied der Akademie, A. V. NIKOLAEV und A. G. ČELIŠČEVA

In unseren vorhergehenden Mitteilungen wurden die Erhitzungskurven, das spezifische Gewicht und die Härte der natürlichen Borate und ihrer Ent-

wässerungsprodukte vor und nach der Boratumwandlung charakterisiert (siehe dieselben Autoren: «Erhitzungskurven der Borate» und «Spezifisches Gewicht und Härte der natürlichen Borate und ihrer Erhitzungsprodukte»).

Jetzt wollen wir einige vorläufige Resultate kalorimetrischer Bestimmungen für Inyoit und dessen Erhitzungsprodukte sowie Röntgenogramme nach Debye betrachten. Wir führten im Kalorimeter von M. S. Wrewski Versuche zur Bestimmung der Lösungswärme des Inyoits und seiner Erwärmungsprodukte in 25%-iger Schwefelsäure durch.

Nach dem Versuche wurde die spezifische Wärme des erhaltenen Systems bestimmt. Die Resultate sind in der Tabelle angeführt.

Lösungswärme des Inyoits in 25%-iger H_2SO_4 (I); Lösungswärme seines Entwässerungsproduktes vor (II) und nach (III) der exothermischen Boratumwandlung

I	$+13\,500 \frac{cal}{mol}$
II	$+56\,200 \frac{cal}{mol}$
III	$-4\,400 \frac{cal}{mol}$

Hieraus erhält man leicht:

a) die Hydratationswärme für Inyoit (die Differenz von II und I) +42 700 cal/mol;

b) die Boratumwandlungswärme (die Differenz von II und III) +60 600 cal/mol.

Bemerkenswert ist die grosse exothermische Umwandlungswärme, was beiläufig auch aus den Erhitzungskurven zu erwarten war. Dort wurde eine spontane Erhitzung des Stoffes um 100—150° mehr, als die Ofenraumtemperatur beträgt, beobachtet.

Somit weisen die Erhitzungskurven, das spezifische Gewicht, die Härte und die thermochemischen Daten alle einheitlich auf tiefgehende Veränderungen hin, die beim Wasserverlust und der Boratumwandlung vor sich gehen.

Ferner nahm auf unsere Bitte hin W. G. Kusnetzow Debyegramme vom natürlichen Inyoit und dessen Entwässerungsprodukten vor und nach der exothermischen Umwandlung auf.

Die Aufnahmen erforderten eine beträchtliche Exposition (bis zu 20 Stunden bei Eisen-Antikathode), was mit den kleinen Atomnummern der in das Molekül eingehenden Elemente zusammenhängt. Da die Resultate ganz unerwartet waren (siehe weiter unten), wurden die Aufnahmen wiederholt, was zur Bestätigung unserer ersten Beobachtungen führte.

Beim natürlichen Inyoit und dessen Produkt nach der exothermischen Umwandlung wurden Röntgenspektren mit einer grossen Anzahl von sehr blassen Linien erhalten. Eingehender werden wir uns bei ihrer Charakteristik nicht aufhalten. Beim entwässerten Produkt, das nicht bis zur Temperatur der Boratumwandlung erhitzt wurde, gaben zwei Aufhahmen, die bei den gleichen Bedingungen gemacht wurden, keine einzige Linie, sondern nur ein schwaches Halo. Mit anderen Worten: wir haben vor uns ohne Zweifel einen amorphen Stoff.

Der Übergang in den amorphen Zustand zeugt vor allem davon, dass Inyoit Hydratwasser hat, was durch eine Reihe anderer Daten bestätigt wird (siehe unsere vorhergehenden Mitteilungen). Das Wasser nimmt am Gitteraufbau teil, und bei dessen Entfernung geht das Gitter auseinander. Das Zeolithwasser geht nicht, wie anzunehmen ist, in die Gitterpunkte ein und deswegen braucht die Entfernung desselben das Gitter nicht zu zerstören.

Die zweite und wohl interessanteste Folgerung bezieht sich auf die Boratumwandlung. Beim Inyoit fürht sie zum Übergang aus dem amorphen

Zustand in den kristallinischen. Hieraus fogt zweifellos ihr exothermischer Charakter: es wird die Wärme bei der Bildung des Kristallgitters aus dem amorphen Stoffe frei. Sie ist ähnlich der Bildungswärme eines Gitters aus einem Jonengase (Born, Haber u. a.).

Auch ihre Nichtumkehrbarkeit wird verständlich. Die Boratumwandlung ist analog dem Übergang einer unterkühlten Flüssigkeit in den kristallinischen Zustand.

Die Existenz des amorphen Zustandes erklärt auch leicht die von uns beobachtete Verringerung des spezifischen Gewichts nach der Dehydratierung. Bekanntlich ist bei der für den amorphen Zustand charakteristischen regellosen Verteilung der Atome die Packungsdichte im Vergleich zu der im kristallinischen Zustande sehr klein. Daher ist im gegebenen Falle das spezifische Gewicht sogar kleiner als bei der Mischung der entsprechenden Oxyde, was von keinem Zerfall in diese Oxyde zeugen kann.

Bei allen chemischen Umwandlungen werden unbeständige Übergangsformen besonders häufig in zähen Mitteln, die die Übergangsgeschwindigkeiten wenig begünstigen, beobachtet. Bekanntlich nahm Wilh. Ostwald an, dass der Übergang von einem Gleichgewichtszustand in den anderen meistens durch eine Reihe metastabiler Formen geht. Im festen Zustand ist der Übergang zu den Gleichgewichtsformen noch mehr erschwert. Die Kompliziertheit des Moleküls begünstigt gleichfalls das Auftreten unbeständiger Formen. Das muss sich insbesondere auch auf die Borate beziehen, wie dies schon Van't Hoff bemerkte*. Daher kann man den beim Inyoit bei der Dehydratation in den amorphen Zustand beobachteten Übergang als typisch für die Borate ansehen. Hiervon zeugt mit aller Eindringlichkeit die Verringerung des spezifischen Gewichts bei der Entwässerung auch bei anderen Boraten. Genau genommen kann man auch einen solchen Fall erwarten, wo die Entwässerung ein unbeständiges kristallinisches Produkt gäbe. Jedoch wird der Übergang in diesem Falle, gleichwie der Übergang des Markasits in Pyrit, nichtumkehrbar sein.

Mit anderen Worten, es ist aller Grund dafür vorhanden, anzunehmen, dass bei den exothermischen Umwandlungen wir es mit Nichtgleichgewichtsformen zu tun haben, im Gegensatz zu den Gleichgewichtsformen bei den gewöhnlichen umkehrbaren endothermischen (bei Erwärmung) polymorphen Umwandlungen. Mindestens findet beim ersten Typ der Übergang aus dem amorphen Zustande in den kristallinischen statt.

Das Ziel der weiteren Arbeiten wird die Aufklärung der Übergangs-Nichtgleichgewichtsformen für die anderen Borate, wie auch für andere Klassen von Stoffen, die nichtumkehrbare exothermische Umwandlungen aufweisen, sein.

Institut für allgemeine und
anorganische Chemie.
Akademie der Wissenschaften der UdSSR.
Moskau

Eingegangen
d. 29. IV. 1937

* Siehe Van't Hoff «Ozeanische Salzablagerungen», aus dem Deutschen übersetzt, unter der Redaktion von A. V. Nikolaev, 1936.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

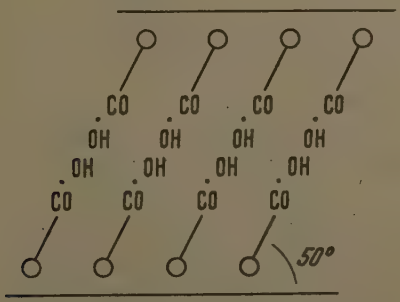
CHEMISTRY

EXPLANATION OF THE DISPOSITION AND INCLINATION OF ROWS OF MOLECULES IN LAYERS OF ORGANIC ACIDS ACCORDING TO ROENTGENOGRAMS

By V. V. ČELINCEV, Corresponding Member of the Academy

The latest roentgenoscopic investigations of layers of organic acids[1-4] have demonstrated that 1) their molecules are arranged in regular rows, the carboxyl groups facing one way and the final methyl radicals fronting the other way; 2) one layer of molecules adjoins an other in strict order, the lines of the carboxyl groups facing each other and thus forming double layers of molecules; 3) the rows of molecules do not run perpendicular to the planes of their layers, as is the case in paraffins, but are at an angle of about 50°.

A picture of the following nature was obtained as a result of roentgenoscopic investigations:

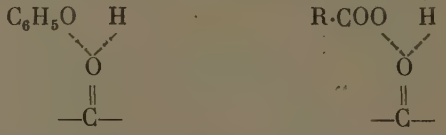


The disposition of the molecules in rows, with the carboxyl groups facing one side and the lines of carboxyl groups in two layers facing each other, has been accounted for, to a certain extent, by the mutual physical attraction of the carboxyl groups; as regards the inclination of the layers of molecules to an angle of about 50°, this has been merely declared to be a curious enough phenomenon, so far unexplained.

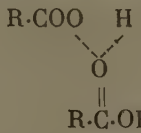
In assuming the physical attraction of the carboxyl groups, proper allowance was not made for the fact that, above all other things, the carboxyl groups, as negative groups giving, within the molecules, dipole moments equal to a 1.7, should rather repel than attract each other, as is considered to be the case in many other instances. Thus, this interpretation as applied to acids is not quite satisfactory.

The explanation of the findings of roentgenoscopical investigations mentioned above, was approached by us from the viewpoint of oxonium forms.

On the basis of an experimental study of the fusibility curves—the eutectic systems—of phenols and acids containing carboxyl organic compounds, we came to the conclusion that the former combine with the latter into definite compounds, which we explain by the ability of acid OH-groups to combine with the higher basic valencies of carbonyl oxygen according to the scheme.



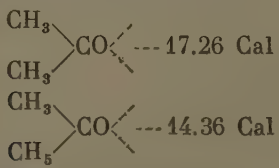
As both acid OH-groups and carbonyl oxygen are simultaneously present in acids, they should, according to our conception, yield the forms:



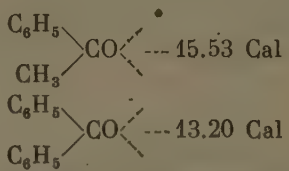
It may be seen from thermochemical determinations that the higher oxonium valencies of the carbonyl groups possess fairly great strength.

Even phenyl radicals exert a very small influence on the manifestation of these valencies, e. g. with the same magnesium-organic alcoholates, as may be seen from the following data:

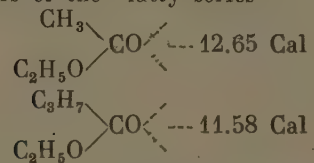
Ketones of the fatty series



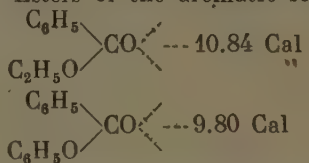
Ketones of the aromtic series



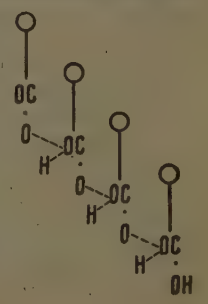
Esters of the fatty series



Esters of the aromatic series



Starting from the forms shown above and bearing in mind the effect of acid hydroxyl groups on the higher basic oxonium valencies of carbonyls, we get an insight into the true nature of the attraction of the carboxyl groups to each other and then on the basis of the same forms, we approach an explanation of the seemingly enigmatic inclination of the rows of molecules towards the plane on which they are situated.



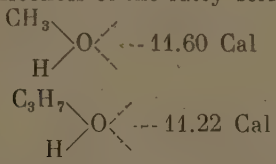
Indeed, if, in the presence of carbonyl groups, the oxygen of the aicd groups starts combining with the former, then one molecule will act on another according to the scheme (on the right):

It is obvious from this scheme why the layers of molecules are inclined with regard to the plane on which they are situated, the latter being given a horizontal direction.

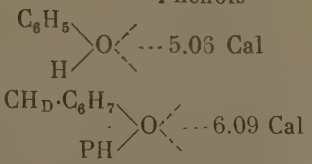
Furthermore, on the basis of the same oxonium forms, one understands the attraction of one layer of molecules of acids by another such layer along the line of the carboxyl groups. The fact is that, if the higher valencies of the carbonyl groups in one row are used up by the combination of molecules with each other, there still remain oxonium valencies, though weaker ones, in the hydroxyl oxygen atoms.

According to our data, the thermal effects produced by simple hydroxyl groups with the same magnesium-organic alcoholates as mentioned above are as follows:

Alcohols of the fatty series

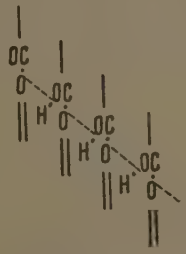


Phenols



Here the influence of phenyl residues, the latter being directly combined with oxygen, is much stronger than in carbonyl compounds, where the influence is via carbon.

In any case, these valencies are amply sufficient for one layer of molecules of acids to be attracted to another such layer along the line of the same carboxyl groups:



As a result of this second attraction, the molecules of acids become arranged in double-layer rows.

Thus, on the basis of oxonium forms, and as a result of a clearer understanding of the attraction of the carboxyl groups to each other, an explanation is found for the inclination of rows of molecules with regard to the plane on which they are arranged in layers, which, up to the present time, has not been accounted for in any other manner.

This tendency of acid molecules towards complex-formation between each other and with water[5] seems to account for their ability of yielding foam, unlike paraffins, in accordance with which the latter, similarly to the higher alcohols do not show any inclination of the molecule rows, so characteristic for acids, in the roentgenograms.

REFERENCES

[1] A. Müller, Trans. Chem. Soc., **123**, 2047 (1923); G. Schearer, ibidem, 3152; A. Müller a. G. Schearer, ibidem, 3156. [2] G. Schearer, Proc. Roy. Soc. A, **108**, 665 (1925). [3] J. J. Trillat, C. R., **184**, 812 (1927). [4] J. J. Trillat. Ergebn. Techn. Röntgenkunde, **2**, 31 (1931). [5] Langmuir, Journ. Amer. Chem. Soc., **39**, 1865 (1917).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

CHEMISTRY

ON THE POTENTIAL DIFFERENCE BETWEEN SOLID SILVER HALOGENIDES AND AQUEOUS SOLUTIONS

By B. P. NIKOLSKIJ and V. M. VDOVENKO

(Communicated by A. N. Frumkin, Member of the Academy, 4. VI. 1937)

Since the time of Haber's (1) classical work it has been universally considered that on the interface:

$$\text{Ag } X \text{ (solid)} \mid \text{aqueous solution}$$

is established a potential difference, expressed by the equation

$$\varphi = \varphi_0 + \frac{RT}{F} \ln a_{Ag^+} = \varphi_0' - \frac{RT}{F} \ln a_{X^-}, \qquad (1)$$

where X is the halogen and a_{Ag^+} and a_{X^-} are the activities of the corresponding ions in solution.

Haber's theory, however, was but approximately verified by few experiments only. The problem of the above-mentioned potential difference acquires a particular interest in connection with two other problems: 1) the structure of the double layer and the absorption of ions in it(2) and 2) the theory of the glass electrode, in which potential difference between the solid and the liquid electrolite is also considered.

Therefore, it seemed of interest to study systematically the relation between the potentials of the solid silver chloride or iodide and the composition of the solution, and besides to endeavour to find such ions, as would influence the potential simultaneously with ions Ag^+ and Cl^- (or I^-) in analogy with the influence, under certain conditions, of Na^+ ions on the potential of a glass electrode. The halogenides of silver are of special interest for this purpose, as the phenomenon of ion adsorption(3), the zero charge point(4) and other properties have been studied in their case.

We have studied cells of the type:

$$\text{Ag} \mid \text{Ag}X \text{ (saturated), solution } Y \mid \underbrace{\text{Ag}X}_{\text{membrane}} \mid \text{solution } Z \mid \begin{matrix}\text{saturated}\\ \text{calomel}\\ \text{electrode}\end{matrix} \qquad (\text{I})$$

where $X = \text{Cl}$ or I, $Y = \text{KCl}$, KI or $AgNO_3$, and $Z = AgNO_3$, KCl or KI.

The solution Y was not subjected to any changes during the experiment, while to the solution Z was gradually added a potassium halogenide solution (if $Z = AgNO_3$) or a silver nitrate solution (if $Z = \text{KCl}$ or KI), same as in ordinary potentiometric titration. Thus, in our experiments the concentration

(activity) of silver and halogen ions varied within a wide range. A chloridyzed (or iodyzed) silver electrode was also immersed in the solution Z.

The potential difference between the latter and the silver electrode of the cell (I) gave the electromotive force of the cell:

$$\mathrm{Ag} \mid \mathrm{Ag}X \text{ (saturated), solution } Y \mid \underbrace{\mathrm{Ag}X}_{\text{solid membrane}} \mid \text{solution } Z, \mathrm{Ag}X \text{ (saturated)} \mid \mathrm{Ag} \quad \text{(II)}$$

Membranes of the solid AgCl were prepared in the form of disks, 2 mm thick and 2—3 cm in diameter, by pouring some molten salt upon a cold steatyte plate, in which corresponding hollows had been made. The AgCl-plates obtained, were fixed to the end of a glass tube (about 1 cm in diameter) either by means of molten silver chloride, or piceine. The membranes of AgI were made by pressing a mixture of AgI-powder and a small quantity of paraffin into tablets. The latter were fitted in to the glass tubes and fixed with piceine.

The solution Y, into which a chloridyzed (or iodyzed) silver electrode had been immersed, was poured into these tubes. The tube with the membrane was then immersed into a small tumbler into which the solution Z had been poured. An agar-agar siphon with KNO_3 was placed into the same vessel to be connected with the calomel electrode.

A compensation method with a binant electrometer as a zero instrument ($\pm$ 2 mV sensitivity), was used for measuring the electromotive force.

According to Haber's theory the electromotive force of the cell (II) must be equal to zero, independently of the composition of the solutions Z and Y. In our experiments it often differed from zero and was equal to several millivolts, but in the process of titration it remained constant within range of the experimental errors (Table 1).

Table 1

Titration of 20 cm³ of 0.01 n $AgNO_3$ (solution Z) with 0.1 n KCl; $Y = 0.1$ n KCl; AgCl = membrane

KCl, cm³	0	0.2	0.4	0.8	1.2	1.6	1.8	2.0	2.4	2.8	3.2	3.6	4.0
Electromotive force in mV in cell II	4	6	7	6	6	3	4	4	4	8	8	8	9

Average—6 mV

The fact that the electromotive force differed somewhat from zero, is most probably due to the non identity of the inner and outer surface of the membranes; this phenomenon is analogous to the «asymmetry potential» of glass electrodes. For some specimens of electrodes, however, this «asymmetry potential» differed but slightly from zero. For the membranes made of AgI this «asymmetry potential» has a considerably greater value.

In accordance with the equation (1) the electromotive force of the cell (I), by Haber's theory, should be equal to

$$E = E_0 + \frac{RT}{F} \ln a_{Ag^+} = E_0' - \frac{RT}{F} \ln a_{X^-} \qquad (2)$$

where a_{Ag^+} and a_{X^-} are the activities of ions in the solution Z.

Consequently, in the process of titration this electromotive force must vary similarly to the silver electrode potential during an usual potentiometric titration. Our experiments, one of which is set forth in Table 2, fully confirm

this conclusion: the titration curves obtained in the above mentioned manner are quite identical with the usual ones (cf. figure, curve *a*).

Table 2

Variation of the Electromotive Force by Titration of 20 cm³ of 0.01 *n* $AgNO_3$ (solution *Z*) with 0.1 *n* KCl with a membrane of AgCl at 18° C

KCl, cm³	*E*, mV	KCl, cm³	*E*, mV
0	433.0	2.0	197.0
0.2	439,0	2.4	143.0
0.4	436.0	2.8	131.0
0.8	429.0	3.2	118.0
1.2	421.0	3.6	113.0
1.6	399.0	4.0	109.0
1.8	373.0	—	—

The conformity of the results of our experiments with Haber's theory may also be demonstrated in the following manner. The constants E_0 and E_0' in the equation (2) are connected with the solubility product *K* AgX of the substance AgX by the formula

$$P_K = -\lg K_{AgX} \frac{E_0 - E_0'}{57.7} \text{ (at 18° C)}, \qquad (3)$$

where the values *E* are expressed in millivolts.

The value E_0 may be obtained by the equation (2) from the experimental data in that part of the titration curves which correspond to the excess of $AgNO_3$, and E_0'—to the excess of K*X*. Consequently, the solubility product of Ag*X* may be calculated by the equation (3) (assuming the activity coefficients to be equal to unity).

Such computations gave

$K_{AgCl} = 1.3 \cdot 10^{-10}$ and $K_{AgI} = 1.2 \cdot 10^{-16}$

in accordance with the data available*.

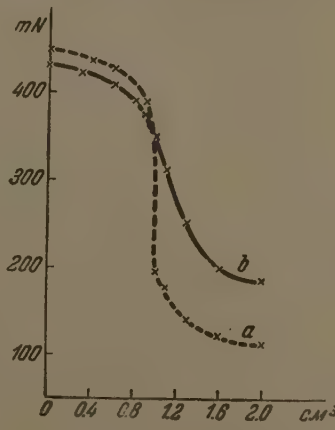


Fig. 1.

The Influence of Foreign Ions. A series of experiments was conducted by us in order to establish the influence of the salts $HgNO_3$, $Pb(NO_3)_2$, $AuCl_3$, LiCl and $TlNO_3$ (AgCl-membranes) and also of KBr (AgI-membranes) upon the electromotive force of the cell (I) by adding them to the solution *Z*.

None of these salts except thallous nitrate proved to have any influence on membrane potential. Preliminary titration experiments of 10 cm³ of 0.01 *n* silver chloride with potassium chloride (0.1 *n*) (with AgCl-membrane) in the presence of thallous nitrate (1.7 g) gave a curve, which sharply differed from the normal one (figure, curve *b*).

It is rather probable that the influence of thallium ions is analogous to that of sodium ions on the glass electrode potential in alkaline solutions. If this effect is confirmed, we may most probably refer it to the forma-

* The data mentioned above refer to one of the numerous experiments made by us. Fuller data may be found in the dissertation of V. M. Vdovenko [5].

tion of solid solutions between AgCl and TlCl, as the shape of the curve shown on the figure can hardly by accounted for by a simple precipitation of TlCl.

S u m m a r y. It has been shown that the potential difference between solid AgCl or AgI and aqueous solutions of salts strictly follows Haber's theory.

N o t e. After this work, the results of which were partly publiched in the dissertation of V. M. Vdovenko, had been completed, Kolthoff's and Sander's work(6) appeared, in which the authors studied the same problems. Their results correspond with ours, excepting thallium salts, which, according to their experiments, do not influence the electromotive force. The divergence from our experiments may perhaps be explained by the application of small concentrations of thallous ions. It is a matter for regret that these concentrations are not shown in their work. The question of the influence of thallous ions therefore requires further investigations.

Laboratory of General and Inorganic Chemistry.
The Chemical Institute of the Leningrad State University.

Received
4. VI. 1937.

REFERENCES

[1] H a b e r, Annalen der Physik, **26,** 927 (1908). [2] F r u m k i n, Ergebn. d. exakt. Naturwissensch., **235** (1928); Журн. физ. химии, V, 240 (1934). [3] L a n g e u. B e r g e r, ZS. f. Elektrochemie, **36,** 171 (1930). [4] F r u m k i n u. O b r u c h e v a, Biochem. ZS., **182,** 220 (1927). [5] V d o v e n k o, Scientific Notes of the Leningrad State University. II, No 11 (1936). [6] K o l t h o f f a. S a n d e r s, Journ. Amer. Chem. Soc., **59,** 416 (1937).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

CHIMIE

ÉTUDE SUR LA POLYTHERME DU SYSTÈME BINAIRE HNO_3 — HCl ET DU SYSTÈME TERNAIRE HNO_3 — HCl — H_2O

Par A. G. KOGAN et V. I. NIKOLAEV

(Présenté par N. S. Kurnakov, de l'Académie, le 5. V. 1937)

Cet article présente une partie de l'étude sur la polytherme du système quaternaire K_2O–N_2O_5–H_2Cl_2–H_2O. Les autres systèmes ternaires, faisant

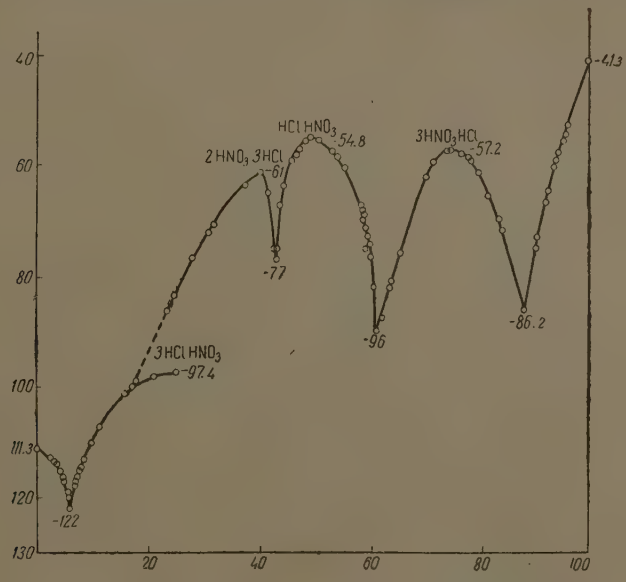


Fig. 1. Système HCl—HNO_3. Diagramme de la fusibilité

partie de ce système quaternaire, ont déjà été élaborés par d'autres auteurs et par nous-mêmes

Des systèmes binaires faisant partie du système ternaire, deux ont été étudiés par d'autres auteurs. Le système H_2NO_3–H_2O a été minutieusement étudié par Pickering et par Kusterkreman. L'étude du système binaire HCl—H_2O faite par Pickering a été continuée par Rupert. La polytherme du système binaire a été étudiée pour la première fois par nous. Nous avons

observé les variations de la température à l'apparition des premiers cristaux du système en question, en changeant la concentration de HCl dans HNO_3 de 0 à 100%. La solution a été refroidie dans le réservoir de Dewar par l'air liquide. Dans le tableau 1 sont données les températures de l'apparition des premiers cristaux aux points les plus importants et leur composition en pour-cent moléculaire et d'après le poids. Ces chiffres nous ont permi

Tableau 1

Echantillons №	Pour-cent d'après le poids		Pour-cent moléculaire		Températ. de l'appar. des crist. °C
	HNO_3	HCl	HNO_3	HCl	
1	0	100	0	100	111.5
2	3.91	96.09	2.30	97.70	112.6
3	9.30	90.73	5.57	94.43	120.0
4	9.64	90.30	5.81	94.18	122.0
5	11.10	88.80	6.74	93.10	117.8
6	24.73	75.35	18.66	84.35	101.4
7	Point de transition		17.54	82.48	99.4
8	Maximum latent		25.00	75.00	—97.4
9	34.10	65.70	23.21	76.91	86.0
10	48.86	51.24	37.76	62.22	63.4
11	53.81	46.28	40.25	59.95	61.0
12	54.32	45.89	40.65	59.35	Précipit.
13	56.36	43.67	42.76	57.24	75.0
14	56.57	47.50	43.12	56.90	—77.0
15	56.88	43.18	43.26	56.75	—75.0
16	62.74	37.27	49.46	50.60	—55.4
17	63.45	36.58	49.91	49.91	—54.6
18	64.36	35.67	51.00	48.83	—55.0
19	67.25	32.91	54.16	45.71	—58.0
20	72.62	27.39	60.54	59.40	—77.8
21	73.48	26.66	61.41	38.50	—90.0
22	75.28	24.77	63.75	36.25	—82.0
23	80.62	19.39	70.64	29.36	—61.4
24	83.46	16.17	74.88	25.00	—57.2
25	90.48	10.06	83.85	16.89	—74.2
26	93.11	7.20	88.15	13.76	—86.2
27	94.23	5.78	90.34	9.59	—75.0

de dessiner le diagramme de la fusibilité représentée sur la fig. 1. Les maxima du diagramme correspondent, comme cela a été confirmé par l'analyse des phases solides, à trois combinaisons aux formules chimiques: $3HNO_3.HCl$, $HNO_3.HCl$ et $2HNO_3.HCl$. De plus, l'analyse de la phase solide et la marche de la courbe ont prouvé la présence de la combinaison $3HCl.HNO_3$, à la fusion au maximum latent. Les combinaisons à la fusion au maximum évident ne sont stables qu'à la température au-dessous de —50°. À la température plus élevée on observe une réaction plus compliquée entre HCl et HNO_3

accompagnée par la formation du chlorure de nitrosyle, de l'eau et du chlore selon l'équation

$$HNO_3 + 3HCl = NOCl + Cl_2 + 2H_2O.$$

C'est nous aussi qui avons étudié pour la première fois le système ternaire HNO_3—HCl—H_2O. En observant la température d'apparition des premiers cristaux de différente composition nous avons obtenu une série de chiffres. Les principaux de ces chiffres sont représentés sur le tableau 2. Ces chiffres

Tableau 2

Echantillons №	Pour-cent d'après le poids			Pour-cent moléculaire			Tempér. de l'appar. des crist. °C
	HNO_3	HCl	H_2O	HNO_3	HCl	H_2O	
1	31.39	1.41	67.20	10.67	9.91	87.42	—46.2
2	4.20	20.21	75.59	1.38	11.51	87.11	—73.0
3	6.48	18.06	75.46	2.15	10.34	87.51	—75.5
4	2.43	24.41	73.16	0.61	14.04	85.15	—71.5
5	12.79	14.49	69.72	4.42	10.46	85.12	—72.0
6	6.44	18.19	75.37	2.14	10.45	87.41	—75.5
7	7.23	16.24	75.83	2.14	9.75	88.11	—75.5
8	3.97	21.69	74.34	1.32	12.45	86.23	—73.0
9	9.45	20.32	70.23	3.27	12.18	84.55	—67.8
10	25.34	22.25	52.41	10.23	15.56	74.19	—48.0
11	22.78	23.33	63.90	8.61	15.83	75.56	—48.8
12	26.37	23.45	50.18	10.88	16.71	72.41	—49.5
13	25.05	23.80	51.15	10.22	16.78	73.00	—50.0
14	25.71	23.62	50.68	10.55	16.75	72.57	—50.0
15	21.07	28.93	50.00	8.87	20.45	70.68	—44.8
16	11.19	38.98	49.83	4.40	25.83	69.77	—32.0
17	33.00	24.00	43.00	13.81	17.36	68.83	—64.0
18	30.10	28.95	40.95	13.26	22.09	64.65	—50.2
19	35.66	27.68	36.66	16.79	22.58	60.68	—73.8
20	36.34	27.32	36.34	17.21	22.36	60.43	—75.0
21	34.43	27.46	11.12	15.62	19.18	65.20	—63.8
22	55.14	16.03	28.83	30.02	15.08	54.90	—52.4
23	51.20	20.89	27.82	28.13	19.43	52.54	—54.0
24	63.48	18.37	18.15	40.00	20.00	40.00	—84.0
25	63.70	19.10	17.20	40.17	20.97	38.84	—78.6
26	39.33	25.43	35.24	18.84	21.48	59.68	—69.0
27	33.07	33.18	33.75	15.86	27.52	56.62	—44.0
28	57.79	37.51	4.70	41.54	46.60	11.86	—79.0
29	56.57	28.96	14.13	35.60	31.45	32.95	—70.5
30	84.46	12.58	2.96	72.61	16.66	10.13	—92.0
31	76.54	15.73	7.73	58.57	20.70	20.73	—78.4
32	67.32	27.74	4.94	50.80	36.17	13.03	—96.0
33	8.43	90.06	1.91	4.93	91.11	3.91	—123.7

nous ont permi de dessiner le diagramme de la fusibilité du système ternaire représenté sur la fig. 2. Comme ce diagramme fait voir, nous avons limité les champs de la cristallisation des composés suivants: la glace, $HNO_3.3H_2O$, $HNO_3.H_2O$, HNO_3, $3HNO_3.HCl$, $HNO_3.HCl$, $2HNO_3.3HCl$, $HCl.3H_2O$, $HCl.2H_2O$ et $HCl.H_2O$. Nous avons lié les maxima de fusibilité par des

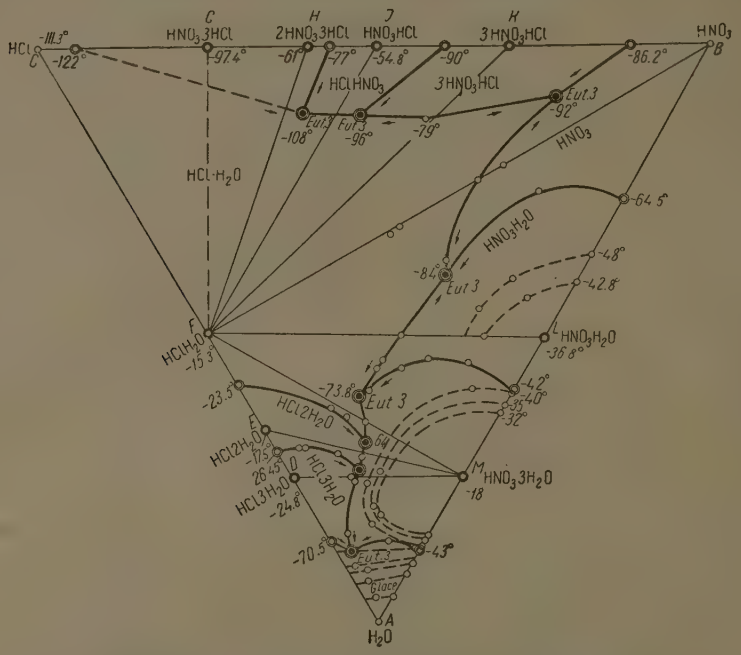


Fig. 2. Le diagramme de la fusibilité du système ternaire HNO_3—HCl—H_2O.

sécantes singulières lesquelles ont divisé le triangle primaire du diagramme en 10 triangles secondaires. Dans chaque triangle secondaire se trouve une triple étoile de rayons avec la température de cristallisation la plus basse et constante. Notre diagramme correspond entièrement aux recherches théoriques de Kurnakov, de l'Académie, exposées dans son article «Topologie des diagrammes chimiques».

Institut de chimie pure et anorganique.
Académie des Sciences de l'URSS.
Moscou.

Manuscrit reçu
le 5. V. 1937.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

CHEMIE

DIE OXYDATION ALS EIN WEG ZUR BILDUNG KOHLEHYDRATISCHER SUBSTANZEN

Von N. A. ORLOV und I. S. MUSTAFIN

(Vorgelegt von N. D. Zelinskij, Mitglied der Akademie, d. 11. V. 1937)

In einer früheren Mitteilung von N. A. Orlov und A. Th. Schalygin(1) wurde bereits bewiesen, dass eine milde Oxydation der unsymmetrischen Diphenyl- und Methyl-Phenyl-Äthylene durch Luftsauerstoff unter Beteiligung alkalischer Kondensationsmittel zur Bildung kohlehydratischer Körper führt. Das Ziel dieser Versuche bestand in experimenteller Bestätigung einer von N. A. Orlov(2) früher geäusserten Vermutung über die Möglichkeit einer Kohlehydratsynthese ohne jede Beteiligung biochemischer Agentien unter Versuchsbedingungen, welche den in der Natur vorhandenen nahe stehen. Das Ergebnis der Untersuchung lässt mit Bestimmtheit einen Schluss ziehen über die Bildung von Kohlehydraten aus dem intermediär bei der Verwitterung (langsamer Oxydation) entstehenden Formaldehyd. Das weitere Schicksal der Kohlehydrate ist mit der Grundfragen der Geochemie des Kohlenstoffs aufs engste verbunden, da, abgesehen davon, ob diese Kohlehydrate einer weiteren Humifizierung, unterliegen oder als Substrate für biogene Synthesen dienen, ihre Rolle immer diegleiche bleibt—der Entwertung der Materie und der Zerstreuung der Energie entgegenzuwirken. Ähnliche Schlussfolgerungen hat auch R. Fosse(3) durch seine Versuche gewinnen können. Es ist ihm nämlich gelungen die Bildung des Formaldehyds neben Harnstoff und Zianwasserstoff in den Produkten der Permanganatoxydation von Glykose, Sacharose, Glycerin, Mannit, Aceton, Essigsäure und Glykokoll in ammoniakalischem Medium festzustellen. Dem oxydativen Abbau schreibt daher R. Fosse nicht nur die Rolle eines die Energie entbindenden Faktors sondern auch die eines für biogene Synthesen wichtige Substanzen bildenden Agens zu. Die allgemeine biochemische Bedeutung der gleichen Untersuchungen veranlasste die Verfasser, die Experimente über dieselbe Oxydation individueller Verbindungen fortzusetzen und dabei solche Substanzen zu wählen, deren Konstitution ihnen eine womöglich leichte Bildung des Formaldehyds gestatten würde. Als solche wurden Allylalkohol, Styrol und Dipenten gewählt, also Substanzen, die eine leicht oxydierbare Methylengruppe in ihren Mollekülen enthalten. Das Styrol wurde aus einer engen Fraktion (140—150°) des Ölgasteeres durch ihre Bromierung und Abspaltung des Broms aus recrystallisiertem Dibromid nach J. von Braun und R. Moldänke(4) isoliert; das Dipenten stellten die Verfasser nach der üblichen Methode aus Terpineöl her(5); Allylalkohol war ein käufliches Produkt. Je ein halbes Grammol der genannten Substanzen wurde in Kolben gesetzt und je 0.5 Mol. Kreide, 40 g

Aktivkohle und 25 cm^3 Wasser in die Kolben zugegeben. Die mit Rückflusskühlern versehenen Kolben waren mit einem Sauerstoffgasometer verbunden und der Einwirkung einer Temperatur von 100—110° in einem Trockenschrank während 816 Stunden ausgesetzt. Der gesamte Sauerstoffverbrauch betrug ca. 13.8 l. Die Oxydationsprodukte wurden sodann mit Wasser extrahiert, der Wasserextrakt filtriert, das Filtrat bis zu einem Volumen von 250 cm^3 eingeengt und mit Salzsäure bis zu einem Gehalt 12% HCl versetzt. Die dabei entstehenden Niederschläge waren abfiltriert und die Salzsäurelösung einer Destillation unterworfen. Die Destillation wurde solange fortgesetzt, bis das Destillat keine Reaktion auf Furfurol mit essigsaurem Anilin mehr nachwies. Die Gehaltsbestimmung des Furfurols im Destillate geschah mittels Diphenylthiobarbitursäure nach Tiščenko und Koškin[6]. Der Gehalt an Pentosen entsprechend der gefundenen Werten für Furfuroldiphenylthiobarbitursäure war für die gesamte Menge angewandter Stoffe ein folgender:

für Styrol	0.01561 g	Pentosen
» Dipenten	0.07559 »	»
» Allylalkohol	0.01603 »	»

Durch die angeführten Versuche ist also die Bildung kolhehydratischer Substanzen bei der Selbstoxydation ganz verschiedener Stoffe, wie Styrol, Dipenten und Allylalkohol, analog dem Verhalten der früher studierten Diphenyl- und Methylphenyläthylen bewiesen.

Es scheint höchst wahrscheinlich zu sein, dass die gesamte Ausbeute an Kohlehydrate eine weit höhere ist, da hier die Bestimmung nur der Pentosen allein vorgenommen wurde. Bemerkenswert ist auch eine gewisse Gesetzmässigkeit an Pentosenausbeuten bezogen auf Grammol der Ausgangsstoffe.

№	Substanz	Ausbeuten an Pentosen %	Ausbeute bezogen auf Grammol
1	Allylalkohol	0.0551	0.0320
2	Styrol	0.0300	0.0312
3	*Unsymm*-Methylphenyläthylen *	0.0301	0.0452
4	Dipenten	0.1112	0.15118

Die Werte zeigen eine gute Übereinstimmung der molekularen Ausbeuten für die ersten drei Stoffe, und eine erheblich grössere für Dipenten, was vielleicht durch das Vorhandensein der ausserhalb liegenden Kohlenstoffatome, welche bei der Oxydation als Formaldehyd abgespalten werden, bedingt ist. Die Erforschung dieser Frage wird von den Verfassern fortgesetzt.

Laboratorium fur organische Chemie.
Staatsuniversität. Saratov.

Eingegangen
d. 11. V. 1937

ZITIERTE LITERATUR

[1] N. A. Orlov u. A. T. Schalygin, C. R. Acad. Sci. URSS, XIV, № 6, 343 (1937). [2] Н. А. Орлов, Химия твердого топлива, VII, 419 (1936). [3] R. Fosse, C. R., **202**, 445 (1936). [4] I. v. Braun u. R. Moldänke, B., **54**, 618 (1921). [5] Siehe z. B. Э. Фрэлих, Практ. введ. в орг. химию. Рига (1912), стр. 163 или М. С. Пешекерова, Практич. работы по орг. химии. Госхимтехиздат (1932), стр. 7 и 13. [6] В. Е. Тищенко и Н. В. Кошкин, Журн. прикл. хим., **7**, 1307 (1934).

* Siehe die erste Mitteilung[1]. Grössere Ausbeute an Pentosen hängt von der längeren Oxydationszeit ab (1200 St. statt 816).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

GÉOLOGIE

UNE NOUVELLE MÉTHODE DE DIFFÉRENCIER LES ROCHES DU SONDAGE A L'AIDE DU COMPTEUR DES GAMMA-IMPULSIONS

Par V. A. ŠPAK

(Prérenté par P. P. Lasareff, de l'Académie, le 3. V. 1937)

Pour avoir une idée sur la nature des roches rencontrées par un forage on fait généralement, à mesure qu'on sonde, remonter des carottes comme échantillons de la roche atteinte. L'extraction des carottes entrave considérablement le procédé de sondage en le ralentissant et le compliquant.

Le traitement ultérieur des carottes extraites consiste en détermination des roches qui les composent. Cette détermination demande toute une série d'opérations, la définition de la roche d'après un seul indice quelconque étant généralement bien difficile, qoique parfois possible.

L'extraction des carottes, méthode courante de la documentation des trous, n'atteint pas toujours son but. En effet, lorsque le trou de sonde traverse des roches poreuses, le rendement en carottes est bein faible. Il baisse parfois jusqu'à quelques unités pour cent de l'étendue traversée. Il va sans dire que la documentation des carottes devient dans ces conditions fort imprécise et dans la coupe dessinée apparaissent des endroits blancs, ne contenant pas de renseignements sur les roches traversées. Cette circonstance est le défaut essentiel de la documentation des trous de sonde d'après les carottes.

Il en résulte un désir bien naturel de déplacer l'étude des roches atteintes par le sondage dans les trous mêmes où la roche reste intacte, en état naturel.

L'introduction du carottage électrique en 1929, dans les mines de pétrole de Grozny, constitue un grand pas en avant dans ce sens.

Je ne veux pas m'occuper ici de la caractéristique du carottage électrique; je noterai seulement que l'application de celui-ci ne permet d'étudier les roches que sous l'aspect de leur résistance au courant électrique qui les traverse.

Le fait que l'étude par le carottage électrique ne porte que sur un seul paramètre, présente le défaut essentiel de ce mode d'exploration. Pour combler cette lacune la maison Schlumberger a introduit, presqu'en même temps que le carottage électrique, l'étude d'un autre paramètre dans les trous de sonde dit «PS».

On peut caractériser PS brièvement comme étude des champs électriques naturels. Jusqu'à l'heure actuelle la nature de PS et les causes de naissance de ces champs ne sont pas encore suffisamment étudiées, car elles sont, selon toute apparence, bien nombreuses. Les effets de la filtration-diffusion, les processus électrochimiques, apparaissant dans les roches pendant le forage, peuvent être la cause de ces apparitions de PS dans les trous de sonde.

C'est pourqoi ce mode est-il employé jusqu'à présent comme paramètre adjoint, qui ne fournit que des renseignements complémentaires à l'étude des coupes de sondage.

En 1935, l'Institut Central de Recherches Géologiques souleva la question de construire des appareils permettant d'étudier d'autres paramètres des trous de sonde, outre la résistance électrique.

Ces paramètres, qui devaient combler la lacune dans le carottage et donner la possibilité d'étudier d'une façon complexe les coupes des sondages, ont été la radioactivité et la sensibilité magnétique des roches.

Le sujet du présent article est justement le carottage radioactif; ou le gamma-carottage, comme il est nommé d'après les rayons appliquées.

Les éléments radioactifs entrent dans la composition de toutes les roches de l'écorce terrestre, quoique en état d'une dispersion extrême. Comme il a été établi par un grand nombre d'études faites sur les roches typiques de différentes régions, les roches éruptives sont pour la plupart supérieures, en ce qui concerne leur activité, à l'épaisseur sédimentaire. Les moins actifs sont le sel gemme, le gypse et les calcaires cristallins purs.

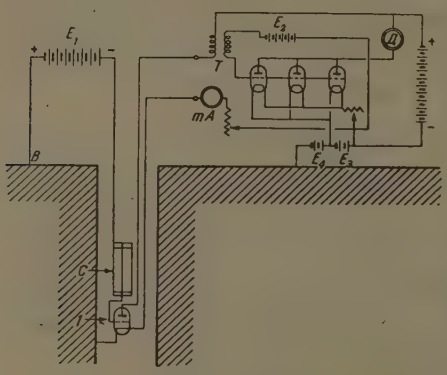


Fig. 1.

Le nombre d'éléments radioacitis d'une roche semble dépendre des processus de formation des roches et des conditions de leur existence ultérieure.

En effet, les observations démontrent que la radioactivité des échantillons d'une roche prélevés de la même formation géologique, varie dans des limites relativement bien étroites. Ce fait permet de différencier les roches d'après leur teneur en éléments radioactifs.

Nous nous sommes servis dans nos études sur la radioactivité des roches de leur gamma-radiation. A cet effet a été employé le compteur de gamma-impulsions (de Geiger-Müller).

La proposition d'utiliser le compteur de gamma-impulsions pour différencier les roches le long du sondage a été faite, en 1934, par G. V. Gorškov et élaborée au cours des années suivantes par Gorškov, Grammakov, Špak, Bočkov, Nikonov et Liatlovskaja. Les appareils de gamma carottage ont reçu la mise au point définitive dans la construction de V. P. Špak.

Ne m'attardant pas à la description détaillée de ces appareils, je me bornerai à donner leur schéma général (fig. 1).

Au compteur C ast amenée la haute tension de la batterie E_1. Le fil du compteur est réuni directement à la grille de la première lampe (I) de l'amplificateur. En passant à travers le compteur C les gamma-rayons expulsent de ses parois les électrons qui produisent l'ionisation du gaz en dedans du compteur. Au moment de l'ionisation, la grille de la première lampe de l'apmlificateur reçoit la charge électrique passée par le compteur. L'accroissement de la tension sur la grille causé par cette charge produit un changement de l'intensité du courant d'anode. Tout ce processus s'accomplit dans un laps de temps très court (dix millièmes d'une seconde), après quoi l'ionisation dans le compteur produite par le passage des rayons cesse et le schéma rentre à son état initial. Ainsi le passage d'un gamma-rayon à travers le compteur produit l'impulsion dans l'anode de la première lampe d'amplifica-

tion, qui s'amplifiant dans la seconde cascade (trois lampes réunies parallèlement) est transmise au compteur electro-magnétique des impulsions (fig. 1, CD).

La difficulté essentielle de réaliser un appareil de carottage à compteur de gamma-impulsions consiste en ce que les charges statiques qui apparaissent sur le fil du compteur à la suite du passage d'une particule ionisante sont très petites et d'une durée trop courte. Il serait impossible de les transmettre sur la surface du sol même à l'aide d'un cable bien isolé.

On a réussi à enlever cette difficulté en introduisant la première lampe d'amplification dans le tube où est placé le compteur (fig. 1). Grâce à cela les impulsions de tension venant du compteur, se transforment en impulsions

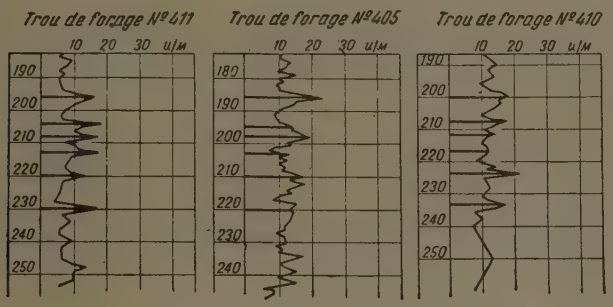


Fig. 2.

du courant d'anode dont la transmission par le cable ne présente aucune difficulté.

Les appareils ainsi construits ont été essayés dans les gisements de pétrole de Syzran, dans les sondages ayant traversé les calcaires du carbon. Cette épaisseur, présentée par les calcaires et les dolomites alternants, est très difficile à séparer par la voie macroscopique. Le seul horizon nettement exprimé ici et pouvant servir d'issue est la suite de marnes et d'argiles, connue sous le nom de l'horizon bariolé et située à la profondeur de 600 m environ de l'orifice du trou de forage.

Or les travaux effectués dans trois sondages de ce gîte avec l'application du gamma-carottage ont établi des horizons assez nets dans des couches supérieures du carbon aussi. Je donne ici des fragments des diagrammes du carottage (fig. 2) et la coupe schématique (fig. 3) que j'ai réussi à construire d'après ces diagrammes.

Les horizons séparés par le carottage sont marqués sur les diagrammes par les lignes noires grasses.

Les essais supplémentaires effectués sur les trous de forage de Vostokoneft ont démontré que pour avoir des idées nettes sur la radioactivité des roches transversées par le sondage à l'aide de notre appareil, il est indispensable de faire sur chaque point des arrêts d'une durée minimum de 10 min.

Le tableau en la page suivante donne les résultats de quelques observations sur les arrêts de différente durée dans un seul point.

Calculons la moyenne d'impulsions par une minute en prenant le plus long arrêt (18.5 impulsions) et comparons ce chiffre à ceux déterminés pour d'autres arrêts plus courts. Nous verrons que la plus grande différence provient des arrêts de 2 et 4 min. (12. 5 et 15.2%). À l'arrêt de 10.7 min. cette différence ne fait que 1%. C'est pourquoi nous acceptons les arrêts de 10 min. comme arrêts minimums.

Durée de l'arrêt en minutes	2.4	4.7	10.7	15.9	21.8	27.1	33.0	38.7	43.4	48.8	58.8
Quantité d'impulsions obtenues	50	100	200	300	400	500	600	700	800	900	1000
Quantité moyenne d'impulsions dans une minute	20.8	21.3	18.7	18.9	18.3	18.4	18.2	18.1	18.4	18.4	18.5
Déviation de la moyenne en % . . .	+12.5	+15.2	+1	+2	−1.1	−0.5	−1.6	−2	−0.5	−0.5	0

Cette règle n'ayant pas été observée dans le trou de forage No 405 (arrêts de 5 min.), la séparation des autres horizons, à l'exception du premier et du troisième, n'a pas été suffisamment précise. Cependant, même un tel dia-

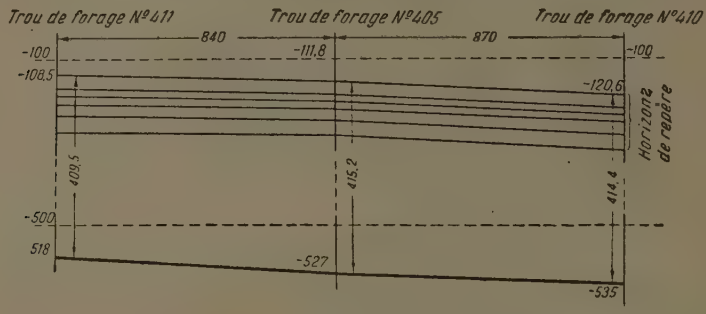


Fig. 3.

gramme permet de trouver des points actifs correspondant à chaque horizon distinctement séparé dans d'autres trous de forage.

Toutes ces données ont été acquises par les tubes de cuvelage, qui ne présentent pas un écran impénétrable pour les gamma-rayons.

A titre de comparaison nous donnons aussi dans le schéma de la coupe l'horizon d'issue des travaux de forage (le haut de l'assise bariolée). Il n'y a de divergence entre cet horizon et les horizons d'issue du gamma-carottage que dans le cas du sondage No 411 (5.5 m); mais l'épaisseur de 400 m peut bien contenir des couches changeant leurs dimensions ou bien s'éteignant tout à fait. C'est pourquoi on ne peut pas s'attendre à la concordance parfaite entre les couches supérieures et inférieures du carbon.

Ainsi, les travaux effectués à l'aide des appareils de gamma-carottage ont prouvé l'efficacité parfaite de ce dernier. D'après toute apparence, la méthode promet beaucoup, vu que sans faire concurrence au carottage électrique elle est apte à résoudre des problèmes inaccessibles à ce dernier (carottage dans des tubes de cuvelage).

De plus, le gamma-carottage donne un paramètre précis et déjà connu (radioactivité des roches), ce que lui permet de participer en même temps que le carottage électrique, aux recherches complexes des roches, en facilitant ainsi la solution du problème du forage sans carottage.

Institut Central
de Recherches Géologiques.
Léningrad.

Manuscrit reçu
le 3. V. 1937.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

GEOLOGY

ON THE AGE OF THE «UPPER SIDERITE CLAYS» OF THE BASIN OF THE RIVER KUBAN (NORTH CAUCASUS)

By N. P. LUPPOV

(Communicated by A. A. Borissiak, Member of the Academy, 4. VI. 1937)

Lower cretaceous deposits of the western part of the North Caucasus (to the west of the River Belaya) are so markedly distinguished from the coeval deposits of the more eastern regions of the North Caucasus as to render a direct comparison with the latter exceedingly difficult.

This circumstance has obliged geologists engaged in the North-West Caucasus to evolve a local scheme of stratigraphy of the cretaceous group. Such a scheme was proposed by K. I. Bogdanovich in 1910—1911 for the Goryachekliuchevskij and Kalužskij regions([2],[3]). This scheme was subsequently adopted by other investigators for the entire North-West Caucasus. The scheme is as follows:

1. Dark streaky clays—alb.
2. Upper siderite clays—apt. and perhaps the Clancy horizon of the lower alb.
3. The Fonar formation; K. I. Bogdanovich—Hauterive, S. I. Charnotski ([15]) and K. A. Prokopov ([7])—Barrem.
4. Lower siderite clays—Hauterivian.
5. Horizon of cloddy conglomerates and dense clays and marls bound therewith—Valangian.

This division was effected on the basis of the litholitic nature of the rocks. The age position of the formation was only partly confirmed by individual mineral finds, frequently of insufficient satisfactory preservation. Hence the age of the formation was not sufficiently founded and parallelisation of deposits in different regions remained, for the most part, provisory.

The age position of the «Upper Siderite clays» was somewhat varyingly determined by different authors. K. I. Bogdanovich ([2],[3]) allocated them to apt; S. I. Charnotski, for the Ilsk region ([15]) and K. A. Prokopov for the Kesslerovo-Varenikovskij region ([8]) noted the presence of Clancy horizon fauna in the upper parts of the layer. For the more western parts of the River Pshekha, I. I. Nikshich and O. S. Vialov([6]), on the contrary, consider the «Upper Siderite clays» beyond the lower part of the apt and above them distingish the «apt sandstone formation», whilst these clays are imputed to the lower apt by A. V. Ulianov([11]).

Several ammonites were found by A. V. Ulianov in 1933—1935 in the «Upper Siderite clays» on the river Kuba (tributary of the river Kurdjips) and on the rivers Pshekha and Pshish. These ammonites, determined by me, permit the presumption that the age of their surrounding strata should be lowered to that of the Barrem([5]). This conclusion found full confirmation in a far richer collection of fauna of ammonites gathered by me in 1936 in these same regions.

The «Upper Siderite clays» in these regions represent a layer of dark-grey clays with bluish shade and with concretions and streaks of siderite. Their depth on the river Pshekha is estimated at 1.175 m by I. I. Nikshich and O. S. Vialov and at 2 000 m by A. V. Ulianov. An horizon of cross bedded sandstones, 10—15 m deep, is observed in the upper surfaces of these clays on the rivers Pshekha and Kurdjips. To the west of this sandstone perhaps corresponds a cluster of lense-like streaks of conglomerates outcropping on the river Pshish at the mouth of the Kura river. The fauna collected originate from two different parts of the section of the clay mass. The composition of the fauna is as follows:

UPPER PART OF THE MASS

River Kuba: *Barremites* cf. *subdifficilis* Karak., *B.* cf. *hemiptychus* Kil., *B.* sp. ind., *Saynella suessi* Simion., S. cf. davydowi Trd.

River Pshekha: *Barremites* cf. *subdiffcilis* Karak., *B.* sp. ind., *Saynella* sp. ind. *Holcodiscus nodosus* Karak.

River Pshish: *Barremites* sp. ind.

LOWER PART OF THE MASS

River Kuba: *Phylloceras* sp. ind., *Barremites (?)* sp. ind.

River Pshekha: *Phylloceras* ex gr. *thetys* d' Orb., *Ph. (Phyllopachyceras)* cf. *infundibulum* d' Orb., *Lytoceras* sp. ind. (ex gr. *subfimbriatum* d' Orb.?), *Barremites* sp. ind. *(tenuicinctus.* Saras et. Schönd?*)*.

River Pshish: *Phylloceras ponticuli.* Rouss., *Ph. (Phyllopachyceras) prendeli* Karak., *Ph. (Ph.)* ex gr. *infundibulum* d' Orb., *Lytoceras* cf. *subfimbriatum* d' Orb., *L.* cf. *densifimbriatum* Uhlig, *L.* n. sp. aff. *puezanum* Uhlig. *Barremites tenuicinctus* Saras et Schönd., *B fallaciosus* Kil. *, *B.* cf. *psilotatus* Unlig. *Subsaynella (?)* cf. *neumayri* Haug, *Holcodiscus* ex gr. *caillaudianus* d' Orb., *Crioceras (Paracrioceras)* ex gr. *emerici* d' Orb., *C. (Paracrioceras ?)* cf. *zitteli* Uhlig.

This fauna gives rise to no doubts as to the age of their surrounding strata. All the forms named are characteristic for the Barrem and it is only individual species which likewise are indicated from Hauterive. The «Upper Siderite clays» developed in the valleys of the rivers mentioned should therefore be allocated to Barrem.

This conclusion also finds confirmation in the fauna contained in the higher and lower strata. The «Upper Siderite clays» in the valleys of the rivers Pshekha and Pshish are underlied by a sandstone clayey mass, the thickness of which was determined at 585—750 m ([6],[11]). In 1934 A. V. Ulianov found, in the upper part of this mass on the river Tushepse (tributary of the river Pshish) *Simbirskites* cf. *discofalcatus* Lah.([5]). Approximately in the same horizon in the upper reaches of the river Kura (tributary of the river Pshish) V. V. Belousov in 1935 found *Simbirskites auerbachi* Eichw.

Judging by the presence of *Simbirskites* the age of the strata underlying the «Upper Siderite mass» may be determined as within the range of upper Hauterive—lower Barrem.

The «Upper Siderite clays» on the river Kurdjips are overlied by a mass of sandstone (thickness 150—175 m) distinguished by S. I. Charnotski([14]) under the name of «brachyopod horizon». These sandstones stretch also further to the west, in the valley of the river Pshekha where they constitute the lower part of the «aptian sandstone formation» I. I. Nikshich and O. S. Vialov([6]). The thickness of the «brachyopod horizon» is determined by A. V. Ulianov at 150—175 m. A collection of fauna of ammonites repesenting the follow-

* This species was originally([5]) determined by me as *Barremites blayaci*, Kil.

ing species was gathered from this horizon by A. S. Muromtsev in 1934 and by myself in 1936:

Puzosia (Pseudohaploceras) matheroni d' Orb. var., *P. (P.) douvillei* Fallot, *Deshayesites* cf. *Iavaschensis* Kas., *D.* cf. *weerthi* Simion., *D.* n. sp. (=*D. weissi* Kil. et Reboul. pars). *Cheloniceras pschechense* n. sp., *Ch. cornuelianum* d. Orb. var., *Ch.* cf. *seminodosum* Sinz.

This fauna leaves no doubt as to the lower aptian age of the «brachyopod horizon».

Thus, according also to its stratigraphical position the «Upper Siderite clays» of the regions under investigation should be allocated to Barrem.

How then can the contradiction be explained between such a determination of the age of this mass and the opinion of previous investigators pointing out its aptian and lower albian forms? Even granting doubt in regard to some of the determinations quoted in literature, the indications of the presence in the «Upper Siderite clays» on the river Psekups and in more western regions of such forms as «*Parahoplites uhligi* Anth.» ([15]), «*Crioceras* cf. *bowerbanki* Sow».([3]), «*Douvilleiceras bigoureti* Seunes», *Belemnites* cf. *semicanaliculatus* Blainv»([8]) and «forms approaching *Deshayesites deshayesi* Leym. and *D. dechyi* Papp.»([4]) can hardly have been caused by confusion of the Barrem species with those of the apt and lower alb.

An explanation for this may be found in changes of facies, i. e. by the transition of sandstone deposits of the apt and lower alb westwards to the facies of the siderite clays.

Investigations on the river Pshisha confirm the presence of such a facial transition. Here the «brachyopod horizon» is absent in its typical form. V. F. Pchelintsev([9]) hypothetically allocates the above mentioned conglomerate outcropping on the river Pshisha nearly the mouth of the river Kura to aptian. However, the discovery of *Barremites* sp. ind. in this horizon and a comparison with the more eastern sections permit the assumption that here we are still dealing with Barrem.

Lower aptian ammonites appear approximately 350 m above this conglomerate. They were found in 1936 by A. N. Afanasyev and myself near the village of Kurinski in the clayey deposits of the topmost part of the lower cretaceous section close by the tectonic contact with the upper cretaceous.

Thus the lower aptian deposits on the river Pshisha transfer to the clayey facies which- judging by indications of the presence of lower aptian ammonites in the clays on the river Psekups([4]) continue also further, westwards.

The same apparently occurs with the deposits of the upper aptian and lower albian which are on the river Pshekha and towards the east represented by a mass of clayey sandstones with globular concretions [«shelly clays with globes», S. I. Charnotski ([14]), the upper part of the aptian sandstone formation, I. I. Nikshich and O. S. Vialov([6])], and to the west, judging by data given in literature, by siderite clays.

The upper border of the «Upper Siderite clays» in different regions therefore run at various stratigraphical levels. A point which still remains vague is whether or not the lower border of these clays also changes its position. I. I. Nikshich and O. S. Vialov([6]) and A. A. Ulianov([11],[12]) compare the sandy-clayey formation underlying the «Upper Siderite clays» on the Rivers Pshekha and Pshish with the «Fonar formation» of K. I. Bogdanovich. This comparison, however, cannot be regarded as proved. The possibitity is not precluded that the sandstones of Mount Fonar represent a higher horizon and perhaps relate to some part or another of «Upper Siderite clays» of more eastern regions.

As can be evidenced from what has been said above, «Upper Siderite clays» in different regions denominate non-coeval deposits. Such sub-divisions,

therefore, as «Upper Siderite clays» and «Fonar sandstones», being, in effect, facial conceptions, should not be identified with stratigraphical units.

In conclusion, a few words regarding the nature of the Barrem ammonite fauna found in the «Upper Siderite clays». As will be observed from the list given above, this fauna posesses a marked expression of Mediterranean form. The greater part of the forms find analogy in the deep water deposits of the Wernsdorf strata of Tyrol and Switzerland. Of the nearer regions a considerable faunal similarity may be observed with regard to the deposits in Rumania and particularly, the Crimea. Barrem deposits similar in fauna on the Caucasus are known in the Gagri region, on the Black Sea coast([16]). Compared with the fauna of the regions named, that of the northwestern Caucasus is distinguished by complete absence of the species *Pulchellia Hamulina* and *Heteroceras*, all very widespread in the Barrem of the Mediterranean province, and also by the rarity of representatives of the species *Holcodiscus*.

Considerably less similarity exists between the fauna of «Upper Siderite clays» and the Barrem fauna of more eastern parts of the Notrh Caucasus([10]). This difference between them may be explained by the varying sea depth in the western and central Caucasus.

A certain part, however, must likewise have been played, in this difference by the elevated district in the region of the river Belaya, the presence of which was marked by V. V. Belousov([1]). It could, to a certain extent, have acted as a barrier, hindering the penetration of deep water Mediterranean fauna into the more eastern regions of the North Caucasus.

The Oil Geological Prospecting Institute.
Leningrad.

Received
4. VI. 1937.

REFERENCES

[1] В. В. Белоусов, Пробл. сов. геологии, VI, № 1 (1937). [2] К. И. Богданович, В отчете Геол. ком. за 1909 г.; Известия Геол. ком., XXIX (1910). [3] К. И. Богданович, В отчете Геол. ком. за 1910 г.; Известия Геол. ком., XXX (1911). [4] Н. К. Игнатович, П. Н. Палей и Н. Н. Славянов, Труды Гл. геолразвед. упр., вып. 102 (1932). [5] Н. П. Луппов, В отчете Нефт. геол.-разв. ин-та за 1935 г. (1936). [6] И. И. Никшич и О. С. Вялов, Материалы по общ. и прикл. геологии, вып. 141 (1929). [7] К. А. Прокопов, Труды Геол. ком., н. с., вып. 112 (1922). [8] К. А. Прокопов, Труды Нефт. геол.-разв. ин-та, сер. А. вып. 71 (1935). [9] В. Ф. Пчелинцев, Известия Геол. ком., XLV, 1, № 10 (1927) (1928). [10] В. П. Ренгартен, Труды Главн. геол.-разв. упр., вып. 63 (1931). [11] А. В. Ульянов, Нефтяное хозяйство, № 3 (1934). [12] А. В. Ульянов, В отчете Нефтяного геол.-разв. ин-та за 1934 г. (1936). [13] А. В. Ульянов, В отчете Нефтяного геол.-разв. ин-та за 1935 г. (1936). [14] С. И. Чарноцкий, Труды Геол. ком., н. с., вып. 65 (1911). [15] С. И. Чарноцкий, Труды Геол. ком. н. с., вып. 91 (1914). [16] М. С. Швецов, Ежегодн. геологии и минералогии, XI, вып. 8 (1910) (1913).

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

GEOLOGY

ON THE MESOZOIDES OF ASIA

By. O. S. VIALOV

(Communicated by A. A. Borissiak, Member of the Academy, 27.VI.1937)

I will first of all deal with some of the basic principles which represent the foundation of my conceptions.

In accepting the conception of the existence of folded zones or orogenesis and platforms, I wish to underline the relativity of these conceptions. One cannot regard platforms as absolute rigid, immutable bodies sharply defined from plastic zones, only the latter being the areas of fold development. Both zones are linked by a gradual transitional, intermediate zone with slighter foldings which gradually smooth down in the direction of the platform. This intermediate, transitional zone does not possess a completely uniform structure along its strike, but at times widens or grows narrower, dislocations in it being defined at times more sharply and at times less.

The causes for such variations are to be sought for in the different depths of deposits, in the lithological composition, in the situation of each given section in relation to the centre of highest tension, etc. Should the platform narrow down, the transitional zones on either side may greatly converge.

Finally, the thought is conceivable, and cases will be cited further on where the folds are developed all over the entrire platform.

Such a paradoxical phenomenen as dislocated platforms may be explained only if we give up the traditional conception of platforms as absolutely rigid bodies and shall consider this conception only as a relative one. Perhaps, in order to avoid the confusion of conceptions, one should not apply the term «platform», with which definite associations are linked. In any event, for localities with placid foldings representing merely relative platforms and dividing the zones of intense folding one could more advantageously apply the term of placid zone.

A fold zone possesses a twin face structure and consists of two branches, in which overthrowing and overthrusts proceed in the direction of the adjacent platforms. These two branches are divided by an intermediate strip «Zwischengebirge» with a more placid folding. The intermediate strip should not however be confused with the placid zone even in the event of convergence of the folded formations. The branches of the fold zone are divergent in regard to the middle strip and anti-divergent in relation to the placid zone. True symmetrical structures of folded zones are not to be found in nature. One of the branches may be developed to a far lesser degree than the other and it is sometimes difficult to state its presence.

Finally, the last statement refers to the significance of mesozoic

shiftings which are frequently, neglected. One can demark regions of widespread development of mesozoic shifts and, moreover, the regions in which the mesozoic folding was the most recent or the last of the most important. Tectonic shiftings which occurred during the mesozoic age, characterizing it in addition to other phenomena (development of the organic world, etc). cannot be regarded as belonging partly to the paleozoic age and partly to the cainozoic. They cannot be regarded as disappearing variscides or emerging alpides. Mesozoic shiftings should be consider as a special mesozoic folding for which the denomination of «Pacific» has been proposed.

The appearance of several mesozoic phases has been established in Middle Asia. For some parts of Middle Asia they are of more significance than the proper alpine phases. Without citing actual material published by several authors confirming their presence and referring back for details to the special work published by me, I will confine myself to the following remarks.

Several indications exist to the effect that the sharp discord universally observed between paleozoic and rhaetic, jurrasic and cretaceous is not caused by variscian folding but by the triassic shiftings corresponding in time to the Indo-Sinic foldings of Indo-China (Fromaget).

I shall now deal with the more general conceptions arising from what has been said above. A long time back, many investigators, beginning with A. D. Archangelskij and N. S. Shatskij have distinguished, in North East Asia, a mesozoic folded zone bordering in the east the Siberian platform. There is no doubt that its continuation to the south-west and further to the west is the Mongolo-Amur orogene of Y. M. Scheinman which possesses a clearly defined bilateral structure. Contrary to the opinion of Scheinman, who assumed that this zone ended in the west and contrary to what is shown on the Archangelski and Shatski's map, I regard the mesozoic zone in question to extend still farther.

The Urals are universally considered as a variscian folded structure. Many even regard the range itself as a morphological unit of paleozoic times, which, in but slighly changed form, has reached our days. Without touching on the assumption of Archangelskij that the principal covering structures of the western slopes of the Urals were created in the lower mesozoic—an assumption, which, in my opinion, generally speaking is most conceivable, I shall deal with indisputable actual material. Jurassic deposits along the eastern slopes of the Urals are greatly dislocated, the dislocation extending in a meridional direction. These facts, long since known, are usually not taken into account in regional formations, perhaps because the mesozoic folding manifestations were generally very little taken into account. Tertiary deposits here lie practically horizontally. Accepting in full the opinion originally uttered by M. M. Tetyaev and supported with some or other changes by other investigators, I assume that the Ural folded zone extends beneath the most recent formations of the West Siberian lowlands far to the east and it is only near the Enisei that it is replaced by the Siberian platform. In distinction, however, from all opinions existing previously, I regard the Ural folded zone as mesozoic, i. e. I assume that in the age of mesozoic folding the Urals were not yet a part of the extensive Russo-Siberian platform.

In view of the mesozoic dislocations in Kazakhstan, Altai, etc. as well as the corresponding alterations of their strikes the Ural folded zone may be combined with that of Mongolo-Amur. We thus obtain a continuous mesozoic structures bordering on all sides with the Siberian platform. We can speak of the Ural-Verkhoyansk mesozoic orogene.

We shall now deal with another zone, the western part of which I have dealt with in detail in my treatise attempting to apply some of Cober's ideas to the Caucasus. This work shows that the Great Caucasus does not belong to the proper Mediterranean folded zone. Showing a southern direction in its shiftings, it pertains to the southern branch of some other folded zone extending parallelly with the Mediterranean one and divided from it by the Trans-Caucasian placid zone. A sharp bend is shown by this branch at the extreme East Caucasus, turning south and forming the Caspian sigmoid. Its further continuation must be sought in the northern ranges of Iran, of which Elbrus likewise has a southernly directed shifting.

As the northern branch of this advance orogene I consider the Donets Basin, which, further on joins with Mangyshlak. Likewise turning south and forming a sigmoid, the northern branch, through the Tuar-kyra folds joins up with the Balkhan and Kopet-dag, in which there is not only clearly manifested the overthrowing of folds to the north, but also the sloping overthrusts have recently been stated in the same direction. Further east this branch passes into Afghanistan and then, rounding the Tadjik virgation in the south, at the Punjab syntaxis stretches across the Trans-Alai range and North Pamir. The overthrow of folds and the overthrusts to the south in South Pamir determines the position here of the southern branch of the advance orogene. Scant explorations of Kuen-Luna and Tibet, where the continuation of this fold zone should be sought, does not allow the exact determination of its position.

Between Ordos and the Yang-tse-Kyang, however, both its branches again become evidently manifest. As regards the western continuation of the Advance (or Caucasian-Pamir) orogene we can, at present, assume conjecturally its possible relation with the Kelets-sandomir dislocations,the Yurski Mts. and the Pyrenees.

The main Mediterranean orogene in Asia stretches across Iran and Afghanistan, but its northern branch passes slightly more to the south than is usually charted. Further it embraces the Trans-Himalayas and, along south Tibet, reaches north-west Yunnan. From here, similarly to the south branch, it alters its direction, closely approaching the meridional one, and contines across Laos. Siam and Cambodia here represent the intermediate (Zwischengebirge) zone of this orogene.

The advance and the main Mediterranean orogenes are divided by a placid zone rather narrow in the west, where it embraces the Caucasus, and greatly widened to the east—in South-Eastern China.

Another placid zone divides the Advance orogene and the Ural-Verkhoyansk one. Very wide in the west, where it is known as the Russian or Eastern European platform, this zone narrows down where the Ural-Verkhoyansk orogene makes a sharp turn to the east. The Caspian sigmoid, by the way, makes such a clear repetition of this bend that the thought arises here of some sort of genetic relation of these phenomena. Serindia and Ordos likewise represent the elements of this Russo-Ordos placidial zone.

A somewhat different, but no less possible formation is conceivable for Eastern Asia.

One may assume the presence of a separate platform in South-East China. Then, in approaching it from the west, Advance orogene divides into two. One of these parts stretches in a latitudinal direction between the rivers Yang-tse-Kyang and Huanhe and then turns north-east towards Sihote-alín. The other deviates sharply southward and stretches into Indo-China; the lower reaches of the River Mekong represent its middle strip. In the case of such a structure the southern (Georgian-Tibet) placid zone also

sharply turns in a meridional direction and approaches to the Bay of Siam. Correspondingly, the Burma ending of the main Mediterranean orogene should be shifted to the west (between the mouths of the rivers Ganges and Solwen). I do not at present dispose of sufficient material to give preference to the first or second assumption.

At the Punjab meridian there occurs a phenomenon known as the Punjab syntaxis. The folds here protrude sharply north and the entire system of folds greatly narrows down. The placid zones narrow down equally. The expression—Narbe, a scar, long since introduced in literature is applicable here not only to the middle bodies lying within orogenes, but perhaps also for the placid zones. In the culminating region, syntaxis, all the zones are narrowed down and compressed to such an extent that all distinctions between the folds and the placid zones pressed between them are smoothed away. This in itself underlines the relativity of the conception of platforms.

There remains one more question which I must presently consider and which, probably has already risen in the mind of the reader namely that there is a certain confusion of the age of folded zones. Indeed, the Ural-Verkhoyansk orogene is clearly defined as a region of mesozoic folding. The nature and relations of mesozoides in the Mediterranean and the Advance orogenes are so greatly darkened by the later alpine folding that it remains uncertain whether they existed as two distinct zones in the mesozoic or represented one continuous zone. By the way, I do not consider the eastern border of Asia, along which stretches the alpine zone and the relation of which with other elements I have not yet succeeded in ascertaining.

It would perhaps be more correct to give map two charts, separately for the mesozoic and the alpine (these will be included in a later article). The first of these maps should reveal the Ural-Verkhoyansk zone of mesozoic structures and the other Eurasian one, in which the mesozoic folding was likewise established. Both folded zones would be divided by the Russo-Ordos placid zone.

The correlation sharply changes in the second chart. The Ural-Verkhoyansk zone does not participate in the alpine folding and, joining with the Russo-Ordos and Siberian platforms forms the unified Russo-Siberian platform.

The Eurasian orogene is clearly divided into two, the Mediterranean and the Caucasian-Pamir or Advance one. The asymmetry of the latter with its transitional character when it approaches to a platform stand out particularly clearlywhen the northern part of its branch practically untouched by the alpine shiftings is considered. It is only in the Punjab syntaxis that this shifting appears in any considerable degree. What is more, the wave of alpine dislocations penetrate here, into the northern platform and the normal structure of the orogene branches is found to be interrupted. The formation of the Tadjik and Kashgar virgations are bound with the reduction of tension along the edge of the syntaxis.

(The present note represents a summary of the report submitted to the XVII Session of the International Geological Congress)

Petroleum Institute
Leningrad.

Received
25.VI.1937.

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2

GEOLOGY

ON STRATIGRAPHIC SUBDIVISION OF THE CONTINENTAL PERMIAN AND TRIASSIC OF THE USSR ON THE BASIS OF THE FAUNA OF EARLY TETRAPODA

By J. A. EFREMOV

(Communicated by A. A. Borissiak, Member of the Academy, 28. VI. 1937)

The studying of early Tetrapoda fauna of the Permian of the USSR has greatly advanced in the course of recent years. It is now possible to distinguish separate faunal complexes and to determine genetic relationships of different forms. New data of the study of the development of the Permian fauna of Tetrapoda of the USSR enable us to approach the problem of individualizing, of definite zones of vertical distribution of forms, i. e. of stratigraphic zones. To render a brief preliminary scheme of such stratigraphic zones is the object of the present paper.

The majority of localities with the Permian faunas of early Tetrapoda are formed by two great faunal complexes—the Kargala and the North-Dvina fauna, consecutively replacing one another in the course of time. The Kargala, or Deinocephalian, Permian fauna has been known for a long time by fragmentary remains from Kargala copper mines (cupriferous sand-stones of the Ural Region). The extremely inaccurate descriptions of this fauna given by old authors, resulted in much uncertainity as to its systematic and stratigraphic position. The works of recent years have clarified this question and have also established the wide spread distribution of the Deinocephalian fauna in the European part of the USSR. The composition of this fauna, as its name shows, is characterized by overwhelming predominance of terrestrial reptiles of the order *Deinocephalia*. The principal representatives of Deinocephalians to be found in the Kargala fauna are the following: *Rhophalodon* — a very primitive form, partly allied to the earliest Gorgonopsians of South Africa, and related also to the large lower Permian Pelycosaurians irom the red beds of Texas; *Deuterosaurus*—a big-sized carnivorous form, fntermediate between the groups of Titanosuchids and Tapinocephalids, similar to but far more primitive than the *Moschosaurus* from the Endothiodon zone of Karroo formation (South Africa); and finally a very large and singular representative of the group of Tapinocephalids—*Mnemeiosaurus*, which seems to anticipate the group of Dicynodonts. There are known also fragments of primitive Dicynodonts, Eosuchians and of an unusual reptile showing convergence with Rodentia, which has been described under the name of Venjukovia.

Later, in this fauna appear real, huge Titanosuchids which I have named *Titanophoneus*, and herbivorous Tapinocephalids—*Moschops*, described by

A. Rjabinin as a new genus of *Ulemosaurus*. The other, more fragmentary remains available, lead us to presume that there is one more representative of Tapinocephalids, close to the genus *Taurocephalus*. There has been furthermore detected a form intermediate between the Deinocephalians, Anomodontians and Dromosaurians, which I have named *Myctosuchus*.

The Stegocephalians of the Kargala fauna are greatly variable and rather numerous. Of these should be mentioned: *Zygosaurus*—a terrestrial Labyrinthodont belonging to the lower Permian American group *Dissorophidae*; *Platyops*—an aquatic carnivorous Stegocephalian, showing a convergence with the recent Gavialians, and *Discosauriscus*, known from the Rotliegendes of Germany, both closely related with the genus *Archegosaurus* from the same Rotliegendes of Germany; *Melosaurus*—an ancestor of Triassic *Mastodonsauridae*; *Chalcosaurus*, related to Condwanian *Brachyopidae*, and possibly, an ancestor of North-Dvina *Dvinosaurus*. Such an abundance of various Stegocephalians may be explained only by the exceptionally favourable external conditions promoting their development, i. e. a sufficient amount of water and comparatively humid climate.

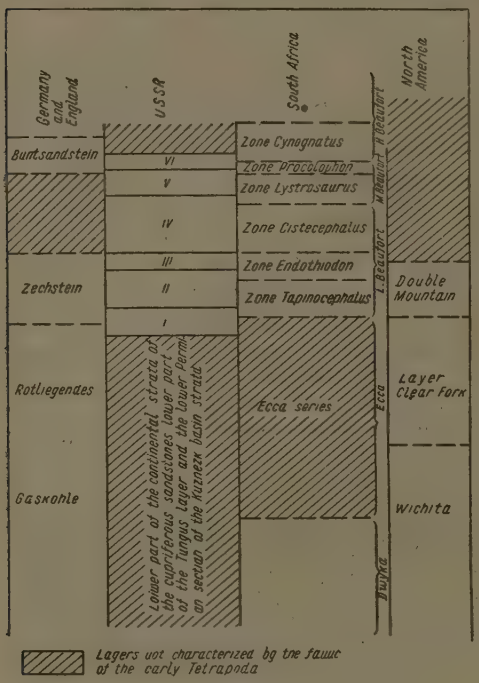


Fig. 1.

The second large faunal complex—the North-Dvina or Pareiasaurian fauna differs considerably from that of the Kargala. First of all, Stegocephalians are represented here by a single form—*Dvinosaurus*, which, owing to the dry climate has become neothenic (sexually mature larva), like the existing Axolotl from Mexico. Deinocephalians are altogether unknown among the North-Dvina fauna—they are replaced by other, considerably less ancient groups of Permian reptiles: highly developed representatives of Pareiasaurids (*Scutosaurus*), true Dicynodontiana, very large late Gorgonopsians (*Inostrancewia* and *Amalitzkia*), highly developed *Theriodontia*; of primitive Cynodontid forms — *Dwinia*, *Permocynodon* and *Anna*. We moreover observe here admixture of forms typical for the North-American fauna — Seymouriamorpha (*Kotlassia* and *Karpinskiosaurus*). The entire complex of forms of the North-Dvina fauna represents a close and comparatively narrow biocoenos adapted to the uniform conditions of riverine existence in a dry, arid region. In this feature it differs from the Kargala fauna, characterized by great variability of forms of adaptation.

The localities with the Deinocephalian fauna are concentrated mainly in the southern and eastern parts of the belt of Permian deposits of the European part of the USSR—in the so-called cupriferous sandstones. They refer to two different stratigraphic zones. The localities of an earlier

horizon, the most ancient of all the localities known in the Upper Permian of the USSR, usually coincide with copper mines of the former Ufa and Perm gubernias, exploited in the 19th century and characterized by copper bearing coarse-grained sandstones and conglomerates, with Ural pebbles alternating with red and reddish-brown hard clays. The large lenses of cupriferous marls of the lower strata of cupriferous sand-stones of the group of Kargala mines in the Orenburg region evidently pertain to this horizon. In these localities have been found the most primitive forms of the Deinocephalian fauna: *Rhophalodon*, *Deuterosaurus*, *Mnemeiosaurus*; of Amphibians—*Discosauriscus*, *Zygosaurus*, *Melosaurus*, *Platyops*. The later forms are met with in the upper strata of the cupriferous marls, in the Orenburg region; in the well known locality near the Isheyevo village (Middle Volga) in the Tartar Republic; in Akbatyrovo mine on the Kityak rivulet; in the region of the middle reaches of the Wjatka river near Malmysh; and near Ochansk, on the Kama.

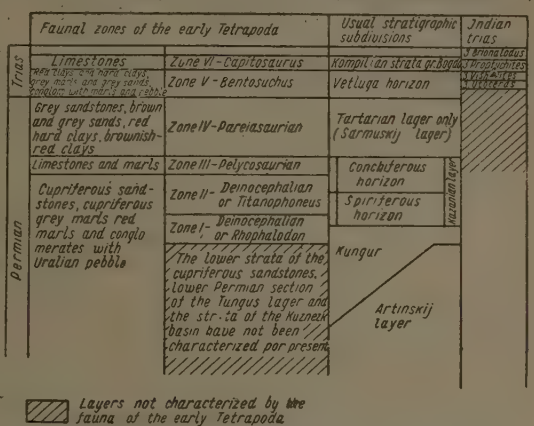


Fig. 2. Approximate Table of the Correlations between the Faunal Zones of the Continental Permian and Trias and the Universally adopted stratigraphic Subdivision of the Sea-fauna.

Separate fragments are met with in outcrops near the Vandovka river and the Kamskye Polyany, on the Kama river, as well as near Kazan (Gorodistshe)—(genera *Titanophoneus*, *Moschops*, *Taurocephalus*, *Myctosuchus*, and Stegocephalians—*Platyops Stuckenbergi*, *Chalcosaurus* and a new species of the genus *Melosaurus*.

Localities with the North-Dvina fauna are spread mainly in the basin of the North-Dvina but, in places, extend southward, appearing in the region of middle course of the Volga (Tetyushi). Most recently, fauna of North-Dvina type, though characterized by the representatives of Dicynodonts of a higher state of development than that of the North-Dvina fauna, and evidently referring to hygher horizons, has been found southward of Orenburg, on the Dongus river.

Considerably less abundant is the newly found Mezen fauna, intermediate in age between those of the Kargala and the North-Dvina. Among the representatives of this fauna are observed very interesting small-sized reptiles of the group *Cotylosauria*, similar to *Procolophonia* but of a most ancient habitus, belonging to two new genera established by me—*Nyctiphruretus* and *Nycteroleter*. Labyrinthodonts of the genus *Platyops (Pl. Watsoni)* more recent than Platyops of the Kargala fauna, as well as doubtless Pelycosaurians found in the USSR for the first time, allied to those of North-America from the Lower Permian of Texas, represented by a new genus *Mesenosaurus*.

The localities of Mezen fauna are known in the Shikhovo-Chirki quarries, near Kirov, on the River Vyatka; on the River Suchona; on the Mezen river, close to where it discharges into the Kimja river, as well as along the whole course of the latter. The above mentioned faunal complexes present sufficient material for an approximate preliminary distinction of large

stratigraphic units i. e. zones. A «zone» must be conceived not as a thin stratigraphic horizon, but as a comparatively long period of existence of a given fauna, frequently embracing an entire complex of different beds.

Faunal zones of the continental Upper Perimian and Triassic of the USSR may be presented as follows (from down upwards). Deinocephalian zone I (or the *Rhophalodon*-zone) embracing the lower horizons of the Cupriferous sandstones, laying below the Belebey series, i. e. corresponding to the Spiripher substage of the Kasanian, or to the Jugow horizon of the Kasanian geologists. The lower part of this zone belongs possibly to the Kungurian.

The upper horizons of the Cupriferous sandstones, the Deinocephalian sands of Isheyevo. the Cupriferous sandstones and marls of the Kityak (Akbatyrowo), and the localities on the Kama in the region of Vandovka and Kamskye Polyany, form the next overlying Deinocephalian zone II (or the Titanophoneous zone).

Both these zones are represented mainly by red and grey sandy-clay sediments and conglomerates with Ural pebbles, characterised by the abundance of copper-ores. Above the red coloured strata of the Deinocephalian zones, in the southern part of the region of Permian deposits (Volga, Ural region, Kama), are usually found chemical sediments, mostly composed of light and pink marls and cave limestones, and in places, with gypsum. From this carbonate series in the region of Kirov, on the River Vyatka, the locality with the fauna of the next, III, or Pelycosaurian zone, is known (Shikhovo-Chirki). In the Northern Region, the III zone is represented by very uniform, red-coloured sandy-clay sediments (Suchona beds of Lutkevich, sandy-marl horizon of the Mezen of Zekkel). Nevertheless by the fauna, they form with the limestones of Shikhovo-Chirki one stratigraphic zone.

North-Dvina fauna composes the next (upward), IV or Pareiasaurian zone. The presence in the red marls of the Vyatka, near Kotelnich, of Pareiasaurians, more primitive than the typical North-Divna Scutosaurs, and provisionally allocated by me to the genus *Anthodon (A. chlynoviensis* n. sp.), indicates the existence of at least two horizons in the Pareiasaurian zone, of which the one nearer to Kotelnich is more ancient than that of the North-Dvina. To this more ancient horizon possibly refers the locality with Pareiasaurian fauna near Gorki. Nevertheless owing to the forms of this locality being still insufficiently studied, this still remains an open question. There remains also as yet unstudied the Pareiasaurian fauna of the Middle Volga in the locality near Tetyushi, which lies, though showing distinct inconformity with, but yet close to the upper Deinocephalian beds developed in the region of Iljinskoje (about 70 m above the latter). The Pareiasaurian or IV zone corresponds in age to the Tartarian sensu stricto, or to the Sarmian series of Masarovich. The possibility is not precluded that the lower layers with more primitive Pareiasaurians lie at the very base of the Sarma series nearly bordering on the Urdjum series. The exploration of the new locality on the Dongus river, to be conducted in the near future, will possibly provide material for distinction of horizons upward of the Tartarian, which up to now have been characterized only by the fauna of Labyrinthodonts.

Comparing the South-African Deinocephalian fauna with that of the USSR, we observe a great many of extremely closely related forms, namely in the Tapinocephalus zone, due to which, in accordance with the opinion of Nopcsa, we may consider the Deinocephalian zones I and II as corresponding in age to the Tapinocephalus zone—the base of the Beaufort

series in South Africa. The presence however in the Deinocephalian zone I of most primitive Deinocephalians similar to ancient Pelycosaurians, such as *Rhophalodon* and *Deuterosaurus*, makes us to admit that at least the lower part of this zone is a more ancient formation than the Tapinocephalus zone, and already partly corresponds to the Ecca series. Among the South African representatives of the fauna of the Tapinocephalus zone, primitive Pareiasaurians *(Bradysaurus)* are known which up to the present have not yet been found in the USSR. Nevertheless when studying the fauna of Deinocephalian zone II, I have come across limb bones evidently belonging to a primitive Pareiasaurian. These bones upon a more detailed study may be determined more precisely, and perhaps will prove to belong to a form related with *Bradysaurus*. Stegocephalians of the Deinocephalian zones I and II are represented by early forms. Thus *Discosauriscus* is characteristic for the Lower Permian of Germany, while *Zygosaurus* is very close to the genus Cacops, known from the upper Wichit beds and from the Clear Fork of North America. According to Romer (with whom, however, I do not agree) the Wichita pertains already to the Carboniferous, and the Clear Fork therefore represent the very base of the Lower Permian.

The absence of Stegocephalians of the group *Dissorophidae* from the Lower Permian of Europe, allows us to suppose that they have migrated from North America somewhat later; and consequently our *Zygosaurus* should be found in layers higher than the Clear Fork. In North America the Double Mountain beds may be considered as such. This statement is in full accordance with the discovery here of *Discosauriscus*, which in Germany extends to the uppermost strata of Rotliegendes and has been found in Monsfeld cupriferous shales. Melosaurus and Platyops represent somewhat more recent forms than Archegosaurus, typical for the Lower Permian of Germany or for the Automnian bands of France, which also proves the correctness of our scheme.

Zone III, or the Pelycosaurian zone, has in South Africa similar forms only from the uppermost beds (Procolophon zone). These latter forms however stand at an incomparably higher stage of evolution than the representatives of the Mezen fauna. Pelycosaurians, found in zone III, are characteristic for the upper strata of the Lower Permian, but in Western Europe they pass also into higher horizons. The fauna of Stegocephalians, represented in zone III by Platyops, clearly characterizes the Pelycosaurian zone as one somewhat higher than the cupriferous sandstones of the zone II.

The position of zone III exactly between the Deinocephalian and the Pareiasaurian zones, enables us to refer it also to the corresponding South-African zone. Thus, the IV or Pareiasaurian zone in all its forms corresponds to the Cistecephalus zone of the Beaufort series, Karroo formation, in South Africa. Subsequently the zone III should correspond to the Endothiodon zone which statement is in accordance with the general age of its fauna.

The correlation of stratigraphic zones of the Permian of USSR are schematically shown in fig. 1.

The next, V or Benthosuchus zone is represented by widely spread Stegocephalians Cocalities in the Wetluga horizon of Fredericks or in the upper strata of Sarma series of Masarovich. The localities of zone V are known on the Upper Volga in the region of Kineshma (Pleso, Semigorye, Reshma); in the vicinity of Rybinsk, on the Vetluga (Zubovskoye, Sludka); on the Unja, on the Kobra (Seryuchan); on the Sharjenga (Wakhnevo), Jug, Lusa; and, lastly,—in the basin of the Mezen and on the Zylma (Ust-Zylma). The fauna of this zone is composed by the new forms of Stegocephalians—

Wetlugosaurus and *Benthosuchus (Benthosaurus)**, which represent the intermediary forms between the rhachitomous and the stereospondylous Labyrinthodonts. The genus *Wetlugosaurus* was recently described from Eastern Greenland, where it is found in the Myalina kochi horizon, above the Eotriassic Proptychites beds. The Greenland *Wetlugosaurus* however is a more progressive form than the typical *Wetlugosaurus angustifrons* from Sludka and Zubovskoje on the Wetluga, and therefore our *Wetlugosaurus* should in any case be placed lower than the Proptychites-beds. This is evident also from a comparison of the stratigraphic position of zone V with that of the last, positively known to be the Triassic VI zone. Zone VI, or Capitosaurus zone is so far known by the fauna of only one locality—the upper limestones of the Great Bogdo mountain, near the Baskuntshak lake Lower Volga Region. Here we meet with two forms of Stegocephalians—*stereospondylous Labyrintodonts* usual in the Lower European Triassic (lower Buntsandstein—*Capitosaurus* and *Trematosaurus*. According to M. Bajarunas's analysis, the Dorycranites fauna of Great Bogdo may be corresponding to the Indian Triassic beginning with the Vishnuites up to Proptychites (including Pseudosageceras) zones. I will add that remains of Trembtosaurus have been found also in India in the Priondotus rofundatus zone.

In any case, the age of the Great Bogdo fauna, according to new nomenclature is also Eotriassic (the Skythian stage). As far as *Wetlugosaurus* is a doubtless ancestor of *Capitosaurus* and in any case represents its earlier rhachitomous form,—as well as its concomitant form *Benthosuchus*, the whole zone V evidently must be corresponding to the very bottom layers of the Eotriassic or to the *Lystrosaurus* zone of the Beaufort series) in South Africa.

It should be mentioned that the fragments of skulls —described by Hartman-Weinberg and Kusmin from Kostroma and from Semigorje and Pless (i. e. zone V), have been erroneously determined by these authors as Trematosuchus and Capitosaurus. I have at my disposal 3 skulls from the same localities, which undoubtedly belong to Wetlugosaurus. The *Lyrocephalus* recently described by these authors also probably from zone V, is likewise a representative of the family *Benthosuchidae*. The skulls of Lyrocephalus from Eutriassic of Eastern Greenland, described by Säve—Söderberg, evidently do not belong to this genus at all.

Received
28. VI. 1937.

* As the generic name «Benthosaurus» given by me in 1929 has been preoccupied (Good and Bean, in 80-s of the last century have described a fish from the family Scopelidae under the name «*Benthosaurus grallator*»), I propose a new name «*Benthosuchus*»; consequently the family *Benthosauridae*, acquires the name of «*Benthosuchidae*».

Comptes Rendus (Doklady) de l'Académie des Sciences de l'URSS
1937. Volume XVI, № 2—7

ZOOLOGY

ON THE DISTRIBUTION OF THE COMMON DOLPHIN (*D. DELPHIS L.*) IN THE BLACK SEA

By V. I. CALKIN

(Communicated by S. A. Zernov, Member of the Academy, 7.V.1937)

One of the least investigated problems of the biology of the Black Sea cetaceans is that of the distribution and migration of the common dolphin. After the investigations of Baer and Danilevskij, a number of writers (Silantiev, Arnold, Dinnik, Malm, Kravčenko) have pointed out the connection existing between the migrations of the doplhins and those of fishes, of which the anchovy (*Engraulus encrasicholus* L.) was considered to be the most important. Kleinenberg, who has studied the food of the common dolphin, has found that it is rather unvaried during the winter months, consisting almost exclusively of the anchovy. On the basis of these observations, Freiman considers that in winter the dolphins concentrate in the regions occupied by the latter.

For the Azov anchovies these regions are the coastal waters of the south-eastern Crimea and the Notrh Caucasus; for the eastern race of the Black Sea anchovy, the Batum region; and for the western race, apparently, the south-western part of the Black Sea. The winter distribution of the doplhin fully agrees with this peculiar distribution of the anchovies.

The distribution of the dolphin in the other seasons of the year remained entirely unstudied till quite recently. The statistics of the catch in the different localities of the Black Sea coast supply no material for the establishment of any regularity in this respect. The specific composition of the catch is, according to Kleinenberg, most varied and does not show the dolphin to be localized at any of the points, as is the case in winter. It is necessary to note here Kravčenko's opinion, who considers the common dolphin to be a purely coastal form, which does not occur in the open sea, and that of Kleinenberg, who believes that this species sometimes occurs in the halistatic region as well.

For a complete elucidation of all these problems, which are of both scientific and practical importance, it was necessary to carry out special investigations, organized on a sufficiently wide scale and ensuring synchronous observations over considerable areas of the Black Sea. The use of vessels for this purpose could not give adequate result, owing to the speed with which the dolphins move. The author, therefore, resorted in 1936 to observations from an airplane.

These observations were carried out systematically for a period of six months (June — November) over the sea surface stretching between the longitudes of Cape Kodor, on the Caucasian coast, and of Cape Sarych, on the Crimean coast. The area surveyed amounted to about 150 000 sq. km, i. e. a little more than one third of the total surface of the Blмck Seea

and included both coastal and halistatic regions. In addition to observations from the flying machine, the author also availed himself of the craft engaged in the dolphin fishing. A whole system of shore observations was also organized at all the main fishing stations.

All these observations carried on for half a year justify the following main conclusions:

1. The common Black Sea dolphin (*Delphinus delphis* L.) inhabits both the coastal and the halistatic regions of the Black Sea, being a typical pelagic species.

2. The dolphins of the species from large accumulations both in the halistatic and coastal regions.

3. Experimental estimations of the magnitude of such accumulations made by counting the separate shoals observed from the plane show them to be very large. So, in the waters of the North Caucasus, the total number of dolphins was estimated at about 250 000—300 000 individuals, while in the waters of the Crimea, it was estimated at about 80 000—100 000.

4. The term «accumulation», is used to denote a group of shoals of different size concentrated over a small area of the sea, thus causing a great density. In the accumulation found off the North Caucasus coast the density was about 1 500—2 000 dolphins to 1 sq. km of the water surface, attaining in places 5 000.

5. The analysis of the composition of the food of the dolphins forming these accumulations shows that the factor controlling their formation is the abundance of food which consists of the Black Sea pelagic fishes: the sprat (*Sprotella spratus phalerica* Risso) and the anchovy (*Engraulus encrasicholus* L.). All the other fishes play but an insignificant role).

6. The accumulations of dolphins concentrating around sprats and anchovies exist for a fairly long time, remaining all the time in almost the same locality.

7. These accumulations result from the concentration of separate individuals or their groups arriving in the region of their food fish.

8. When the food fish of the doplhin is not concentrated, the dolphin is fairly evenly distributed over considerable areas. The movements of the shoals bear then the character of migrations controlled by the search for food. In such periods markedly increases the significance of the following organisms: *Syngnathidae*, *Gadus euxinus* Nordmann, *Trachurus trachurus* L., *Mullus barbatus* L., *Pelamys sarda* Btock, *Idothea algirica* Lucas *Crangon crangon* L.

9. The magnitude of the dolphin shoals is controlled by food conditions. The shoals are the largest when their food is concentrated. On the contrary, when the food fish is sparse, small shoals and solitary individuals prevail.

10. Analyses of the age and sex composition of the catches in the coastal zone show, according to Nikolskji, a decrease in the number of pregnant females and the young in June—July. Observations from the plane and from vessels, which have revealed numerons shoals in the open sea consisting of females and recently born young, justifies the conclusion that during breeding the females keep far from the shores.

11. The migration of pregnant females to the open sea appears to be due to hydro-meteorological factors. During the summer months, roughness of the sea is mainly due to local offshore winds, which do not affect the distant areas of the sea, where calm weather prevails. Breeding in the zone of calm water secures for the new-born dolphins favourable conditions for their first intake of air.

All Union Scientific Research Institute
of Marine Fisheries and Oceanography

Received
13. I. 1937.

PRIX D'ABONNEMENT

Un an — 36 livraisons . . . . . $ 15
Six mois — 18 livraisons . . . $ 7.50
(Séparément $ 0.50 le numéro)
«Nouvelle Série» pour 1933 — 6 livraisons . . . $ 2
«Nouvelle Série» pour 1934 — l'année complète épuisée; volume III (9 livraisons) et volume IV (9 livraisons) en vente à $ 3 le volume.

URSS — Mezhdunarodnaja Kniga, 18, Kuznetskij Most, Moscou (Compte courant n° 263 Banque d'Etat de l'URSS, 12, Neglinnaja, Moscou).
NORTH and SOUTH AMERICA — BOOKNIGA CORPORATION. 255 Fifth Avenue. New York, N. Y.
GREAT BRITAIN — W. H. SMITH & son, Ltd. Strand House, Portugal St London, W. C. 2.
FRANCE — MESSAGERIES HACHETTE. Service Abonnements. 111, Rue Réaumur. Paris, 2e.
SUISSE — Administration du Journal „LE TRAVAIL". 39, Rue de Lausanne. Genève.
ROUMANIE — Deposit de Ziare Luvru. Calea Victoriei 30. Bucarest.
Č. S. R. — MELANTRICH, Akc. Spol. Knihkupectvi — odd. slovanskych knih. Vaclavské nam 42. Praha II. (Ucet post. spor. 20, 208).
BELGIQUE — LIBRAIRIE A.U.S. 38. Vieille Halle-aux-Blés. Bruxelles (C. C. P. 1861. 15 P. Driessen).
CHINA — AMERICAN BOOK & SUPPLY Co 841 Bubbling Well Road. P. O. Box 1798. Shanghai.
HOLLAND — J. GINSBERG. University Bookseller. Kort Rapenburg, 17. Leiden
LIETUVA — „MOKSLAS". Knygynas. Laisves Aleja, 46. Kaunas.
TURQUIE — LIBRAIRIE HACHETTE. Succursale de Turquie. 469, Avenue de l'Indépendance. Boîte Postale Pera 2219. Istanbul.
POLSKA — GEBETHNER & WOLFF. Filja I. Krakowskie Przedm. 15. Warszawa.
ROSSICA. Chmielna 5. Warszawa.
KSIEGARNIA GIRSZOWSKIEGO. Zamkowa 13. Wilno.
PALESTINE — SAFRAN Co. Jaffa Rd. 36. P. O. B. 223. Haifa.
BULGARIA — T. F. TSCHIPEFF. Buchhandlung. Boulevard Dondoukoff 20/22 Sofia. (Postscheckkonto-Sofia 540).
SVERIGE — C. E. FRITZE'S Kgl, Hofbuchhandlung. Fredsgatan, 2 Stockholm.
LATVIJA — A./S. VALTERS un RAPA. Teatra iela Nr. 11. Riga (Pasta tek. rek Nr. 675)
NORGE — JOHAN GRUNDT TANUM. Tidligere Aschehougs Boghandel. Karl Johans gt. 43. Oslo.

Les «Comptes Rendus», largement expédiés à l'étranger dans les centres scientifiques les plus importants et dans les bureaux de nombreuses revues, sont le seul organe scientifique en URSS, donnant tous les dix jours un compte rendu des plus récentes données de la science soviétique.

Prix — $ 0.50